RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Division Activities

The Rubber Division of the American Chemical Society

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International Rubber Congress

At the International Exposition of Arts and Crafts to be held in Paris in 1937, there is to be an International Rubber Congress, which is being organized by the Association Française des Ingenieurs du Caoutchouc et Autres Matières Plastiques.

Though the final program is by no means completed, it is definitely announced that the rubber meetings will be held on June 28, 29, and 30. It is especially desired that papers on (1) the development of new products from latex; (2) synthetic rubber, and (3) rubber derivatives be presented, and it is hoped that rubber chemists and technologists will welcome the opportunity to present papers in these fields and exchange ideas with their colleagues. However, papers need not be restricted to these three subjects, and papers on other chemical or technological subjects will be gladly accepted.

It is further suggested that an American rubber chemist and technologist be chosen to organize an American delegation, and that arrangements then be made with the French Association in order to facilitate the comfort and convenience of the delegates in settling in Paris and in attending the Congress on Rubber.

Every effort will be made to aid American chemists through reduced railway fares, advance arrangements at hotels, attendance at the Congress without expense, and invitation to a grand banquet at the termination of the meetings.

This is certainly a cordial invitation, and it is hoped that at least a few members of The Rubber Division will be able to arrange a trip to Europe so that they can take advantage of this sincere attempt to bring together the rubber chemists of all lands.

A Summary of Current Literature on the Chemistry, Technology, Engineering, Manufacture, and Uses of Rubber and Its Products

It is felt strongly that rubber chemists and technologists in the United States are far too unfamiliar with the "Summary of Current Literature," published monthly by The Research Association of British Rubber Manufacturers. This summary is composed of abstracts of all significant journal articles and patents on rubber chemistry and engineering, from plantation problems through the industry to the finished products.

These abstracts are excellently written, and their authors show great skill in giving in clear and concise form the essential features of the articles and patents.

To show better the scope of the abstracts, the following tabulation gives the subjects covered.

Planting;
Latex;
Raw rubber;
Gutta-percha, balata, etc.;
Compounding ingredients;
Fibres and textiles;
Vulcanized rubber, including:
  Properties and testing,
  Treatment,
  Various products:
    Tires,
    Belting,
    Cables, electric insulation,
    Footwear,
    Games' and sports' accessories,
    Hose, tubing, miscellaneous,
    Mechanical goods,
    Roads, flooring, matting,
    Surgical goods,
    Composite textile-rubber goods,
    Sponge,
    Hard rubber;
General processes and materials,
Machinery and appliances.

Many of the abstracts are non-chemical, and deal strictly with mechanical engineering. For this reason these abstracts cannot be found in *Chemical Abstracts*, which professedly omits articles which do not deal with chemistry, directly or indirectly. Nevertheless these engineering articles and patents are so closely allied to the chemistry and technology of rubber that a rubber chemist who desires to keep abreast of developments in the general manufacture of rubber can ill afford to remain unfamiliar with technological and engineering progress.

There is no convenient summary of developments in the chemistry, technology, and engineering of rubber published in the United States, but this now seems unnecessary, for one need only turn to our colleagues across the ocean and follow their "Summary of Current Literature," which is certainly the last word at present in its intended field. We urge all rubber chemists and technologists to examine this publication, and to decide for themselves whether they will thereafter rest content without it.

Any information which is desired may be obtained by writing to The Research Association of British Rubber Manufacturers, 105 Lansdown Road, Croydon, Surrey, England. It will be a great pleasure for the staff of RUBBER CHEMISTRY AND TECHNOLOGY if there is some response to this suggestion, for The Research Association of British Rubber Manufacturers deserves the greatest encouragement and aid in a material way for the splendid work which is being undertaken. Let us therefore make an effort to help them.

New Books and Other Publications

Malayan Agricultural Statistics—1935. D. H. Grist, Department of Agriculture, Straits Settlements and Federated Malay States, Kuala Lumpur, 1936. Paper, $6^{1}/_{2}$ by $9^{1}/_{2}$ inches. 89 Tables. Two charts. Price 50 cents.

This is the fifth annual summary of Malayan agricultural statistics, and gives data to the end of 1935. It furnishes a useful summary of local information regarding agricultural conditions in Malaya, including a résumé of rubber plantation statistics and activities. [From the *India Rubber World.*]

Diseases and Pests of the Rubber Tree. Arnold Sharples. The MacMillan Company. 480 pp. $8.75.

This book is divided into three parts: General Remarks on Plant Diseases, Structure, Reproduction, and Physiology of Fungi; Form and Function; Diseases and Pests, any one of which may be read independently of the others. Although the subject matter for the most part is intricate to the layman, the author has taken every care to give the simplest and barest outlines compatible with utility. As the late head of the Pathological Division, Rubber Research Institute of Malaya, and formerly Government mycologist, Department of Agriculture, S.S. and F.M.S., Dr. Sharples is well qualified to handle the subject, which is largely based on the results obtained at the R.R.I. since 1931. Although written for embryo and experienced planters, the book should prove of interest to those interested in the general subject of crude rubber. [From *The Rubber Age* of New York.]

The Genus Hevea—Mainly the Brazilian Species. (A reprint.) Adolpho Ducke. Y. G. Aranjo and Co., Manaos, Amazon, Brazil, S. A. 36 pp.

Reprinted from the December, 1935, issue of the *Archivos do Instituto de Biologia Vegetal,* this article presents the results of a study on the natural system of the Amazonian rubber trees according to observations made in the field and not alone on the herbarium samples accepted by most botanists. The various types of *Hevea* trees in the Amazon valley are named, locations given, and each is discussed as to its commercial value. [From *The Rubber Age* of New York.]

1935 Bibliography of Rubber Literature (Excluding Patents). Compiled by D. E. Cable. Including Directory of Rubber Chemicals. *The Rubber Age,* New York, 1936. Price $1.

This is the first of a series of annuals designed to serve the rubber industry by a sustained bibliographic service. The plan cannot fail of appreciative support, particularly by chemists, technologists and those engaged in rubber research.

Section I of the book comprises a list of titles covering the world literature on rubber, classified in a series of 74 separate and distinct bibliographies arranged in a numbering system easily followed, permitting cross-referencing and the preparation of author and subject indexes, which conclude the first section.

Section II is a rubber chemical directory listing brand names of rubber chemicals and other materials commonly used in rubber compounding, classes of chemicals, and addresses of chemical concerns serving the rubber industry. [From the *India Rubber World.*]

Compounding Ingredients for Rubber. Compiled by the Editors of the *India Rubber World.* Published by Bill Bros. Publishing Corporation, New York. 225 pages, with index. Cloth bound, $5'' \times 7''$. $2.50 postpaid in U. S. A., $2.75 elsewhere.

This handbook aims to provide rubber technologists with information about the composition, properties, and uses of all commercial substances employed in com-

pounding. The material presented was solicited from the manufacturers of the various ingredients, and as a result it has the fault of giving the good features of the products and omitting their bad features. In some cases this has led to questionable assertions or even misstatements of fact. The handbook also omits numerous well-known ingredients, such as glue, magnesium carbonate, blanc fixe, liquid asphalts, mineral oil, and others. Some products are badly classified, for example, lime, litharge and magnesium oxide as fillers, lead oleate as a softener, aluminum flake as a reënforcing agent, etc. Nevertheless the book should be of considerable interest and utility to many chemists.

This manual shows strikingly the great number of products at the disposal of the rubber compounder, the difficulty of having an intimate knowledge of them all, and the greater difficulty of obtaining reliable and unbiased information about them. [G. G. HAWLEY.]

Development of the Banbury Mixer. General Atlas Carbon Co., 60 Wall St., New York, N. Y.—This folder contains a letter account by Fernly K. Banbury, giving the interesting story of his invention of the rubber mixer which bears his name. [From the *India Rubber World*.]

A.S.T.M. Standards on Textile Materials. The American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa. 296 pp. $2.00.

In addition to all A.S.T.M. standards on textiles (42 in all), this revised and amplified edition, sponsored by Committee D-13 on Textile Materials, includes a proposed potassium dichromate oxidation method for the determination of total iron in asbestos textiles, a psychrometric table for relative humidity, a section comprising many excellent photomicrographs of common textile fibres and a convenient yarn number conversion table. For the first time new methods of testing, applying to pile floor covering, fineness of wool, corded cotton gray goods, among others, are presented. Changes in standards since the 1935 edition are also included [From *The Rubber Age* of New York.]

A.S.T.M. Standards—1936. (In Two Volumes.) The American Society for Testing Materials, 260 South Broad Street, Philadelphia. Blue cloth binding. Either volume, $7.50; both volumes, $14.00.

These standards are issued triennially, and are supplemented by annual compilations. The 1936 issue comprises two volumes, Volume I giving in their latest form all A.S.T.M. standards covering metallic materials, and Volume II giving those relating to non-metallic materials, including rubber products, electrical insulating materials, and waterproofing materials. In each volume the specifications for a particular class of materials are given first, followed directly by the test methods, definitions, etc. A complete subject index lists each standard with the key-words in alphabetical sequence. The index, plus two tables of contents, one listing standards by materials covered, the other in order of sequence of the serial designations, facilitates the use of this edition. Volume I covers 181 standards; Volume II, 335 standards. Both volumes aggregate 2400 pages. [From *The Rubber Age* of New York.]

A.S.T.M. Standards on Electrical Insulating Materials. The American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa. 326 pp. $2.00.

The 1936 edition of these standards contains 25 testing methods and 10 specifications and includes a number of revised test methods covering the following: varnishes, solid filling and treating compounds, sheet and plate materials, natural mica, untreated paper, insulating oils, and varnished cloths and tapes. Revised specifications appear on friction tape, black bias-cut varnished tape, and asbestos

yarns, tape and roving. Prepared by Committee D-9 on Electrical Insulating Materials, this latest edition of the standards also includes the 1936 report of that Committee, and outlines the research and standardization work currently being carried on. [From *The Rubber Age* of New York.]

Handbook of Chemistry and Physics. 21st Edition. The Chemical Rubber Publishing Company, Cleveland, Ohio. 2028 pp. $6.00.

This twenty-first edition of the Handbook represents a 23-year accumulation of data for the scientist and engineer, brought completely up-to-date, and contains 64 pages more than the preceding volume. Several changes have been made, including a revised (and improved) form for the numerical tables in the Mathematical Section, as well as an enlarged photographic section. For convenience, the Handbook is divided into five sections: Mathematical Tables; Properties and Physical Constants; General Chemical Tables; Heat, Hygrometry, Sound, Electricity, and Light; and Quantities and Units—Miscellaneous Tables. These Handbooks are prepared by a group of collaborators and contributors, with Charles D. Hodgman as Editor-in-Chief. [From *The Rubber Age* of New York.]

Chemical Synonyms and Trade Names. 4th Edition. William Gardner. The Technical Press, Ltd., London, England. D. Van Nostrand Co., Inc., New York City. 496 pp.

More than 25,000 definitions and cross-references of chemical synonyms and trade names are in this book, described as "a dictionary and hand book" by the publisher. This edition is the largest to be published in the series, and supplies a ready reference to names and definitions of raw materials, mineral explosives, dyestuffs, alloys, and commercial chemicals employed in the various branches of industrial chemistry. Many of the definitions contained in previous editions of this work appear in revised or extended form, and hundreds of new names and terms have been added. Although the definitions and cross-references have a decidedly foreign tone, this latest edition should prove an interesting addition to chemical libraries. [From *The Rubber Age* of New York.]

Chemical Engineering Catalog—1936. The Reinhold Publishing Corporation, New York City. 916 pp.

With the 1936 edition of the "process industries' catalog," the Chemical Engineering Catalog "comes of age," this being the twenty-first annual edition. It is larger by approximately 50 pages than the previous edition. The innovation introduced last year of permitting the inclusion of complete catalogs prepared individually by the firms concerned, although the basic principle of restricting copy to actual technical data has been closely adhered to, has been continued in the latest number, as has the separate index of laboratory and reagent chemicals in the Chemical Section. The 1936 catalog, as usual, consists of an alphabetical index, trade name index, equipment and supplies section, chemicals and raw materials section, manufacturers' catalogs, and a section devoted to a list of technical and scientific books. [From *The Rubber Age* of New York.]

Le Caoutchouc. P. Bary. 2nd Ed. Dunod, Paris, 1936. 346 pages.

This new edition of the well-known work by Bary makes available, to those who read French, an up-to-date treatise on the chemistry and physics of rubber and the chemical engineering of the chief processes (vulcanization, incorporation of pigments, reclaiming, etc.) through which rubber passes. The chapter on pigments is new, and it covers the most recent contributions to the subject. The other chapters are equally informative, and they discuss the most important progress of the last few years. The book is an excellent piece of work, and it will certainly be useful to every chemist concerned in any way with rubber. The production engi-

neer will likewise be able to obtain a good impression of recent research and a more comprehensive and more scientific idea of the physical and chemical changes which rubber undergoes during its manufacture into finished products and during the service of these products.   [From *Chimie & Industrie.*]

The Components of Hevea Latex

Part I. The Isolation and Quantitative Determination of the Components

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Introduction

It is noteworthy that the very considerable body of published work on the chemistry of Hevea latex contains no record of attempts at a definite analysis of this complex mixture of substances. This is the more remarkable since it is well known that certain non-rubber components, which have been repeatedly shown to occur in latex, exert a profound influence on the properties of plantation rubber.

A review of the literature shows that evidence has been adduced for the presence in latex of no fewer than sixty different substances, but of these, very few have actually been isolated from latex and submitted to a severely critical examination. In the discussion even of the better-known non-rubber components, such as the sugars, the proteins, the inorganic salts, and above all, the so-called "resins," there is always a certain amount of assumption and inference; and although more or less reliable determinations of the amounts of these components have been made, little is known of their mode of occurrence, or in most cases of their chemical composition. Moreover, an important group of ten to twelve substances, including the fat acids and the natural antioxidants of rubber, isolable from the acetone extract of crepe rubber, have not up to the present been isolated from latex itself, although their presence therein must clearly be inferred.

The present work describes a method for the isolation and quantitative determination of the components of Hevea latex (including rubber hydrocarbon) in the form in which they occur naturally. Such an analysis is necessarily a long and tedious process, involving as it does the isolation in a pure state of a considerable number of highly complex substances, but already the broad outlines of the constitution of this latex have been determined, and the existence of three hitherto unknown components has been established.

It is hoped in the near future to report the results of more detailed chemical investigations of the various components. Further it may be mentioned that applications of the method which are now in hand promise to throw light on a number of vexed questions. These include not only matters of immediate interest to the producer and the consumer of plantation rubber, such as the causes of variability, the constitution of clonal latices, and the effect of ammoniation, but also a group of fundamental problems including the structure of rubber hydrocarbon and the place of latex in the metabolism of the Hevea tree.

Experimental

General.—Two fundamental requirements in undertaking this analysis are, first, that the raw material should be exposed to the least possible risk of undergoing fermentative changes, and second, that throughout the process any treatment, chemical or physical, which might be suspected of effecting chemical change

in the latex or in its components should be avoided. It is felt that the procedure now to be described meets these requirements with a considerably greater degree of success than has hitherto been attained in the handling of the "total solids" of latex.

Drying of Latex.—By arrangement with a nearby estate, the latex from a particular "task" is being submitted regularly in an untreated condition directly from the tapper to the Institute. On days when an analysis is commenced, this latex, immediately on arrival, is passed through a Monel metal sieve, and 1000 grams, in 100-gram portions, are immediately transferred through a burette to ten sheets of plate glass, each 54 cm. square. Each sheet is mounted in a substantial wooden frame to facilitate handling and levelling operations. The latex is then carefully distributed so as to cover almost the entire surface of the glass in a more or less uniform film, which thus averages 0.34 mm. in thickness. The frames are then exposed in the shade to a brisk current of air from a portable fan until the contents have reached a uniform translucence. As each frame attains this state, it is placed in direct sunlight for half an hour to complete removal of water and give a tough transparent film. By this procedure the entire operation of drying one liter of fresh field latex at atmospheric temperature is usually complete within three and one-half hours of receipt of the latex.

Dispersion of the Dried Film.—The dried films are removed from the frames in narrow strips, care being taken to avoid massing. As each strip is removed, it is placed in an aluminum or a glass vessel containing a mixture of carbon tetrachloride (7000 cc.) and acetone (4500 cc.) which is kept well stirred during the operation and at intervals for some time afterwards. In this way a uniform dispersion of the total solids from the original liter of latex is obtained in a remarkably short time, the process being virtually complete in 1–2 hours. At this stage the dispersion is conveniently allowed to stand overnight in the closed vessel.

The use of the above-mixed solvent has the additional advantage that the resulting dispersion is markedly less viscous than dispersions obtained with ordinary rubber solvents.

The dispersions thus obtained normally vary in concentration between the limits of 2.6 per cent (latex total solids 30 per cent) and 4 per cent (latex total solids 46 per cent), but it was judged advisable to use the above standardized procedure rather than to prepare day by day solutions of a fixed concentration and varying volume. The justification for this procedure will appear in the following.

Removal of Rubber.—Acetone (4500 cc.) is now added slowly in a uniform stream to the homogeneous dispersion, which is kept vigorously stirred. The rubber is thus quantitatively precipitated in a fine flocculent form, carrying with it all the proteins, sugar, quebrachitol, and inorganic components of the latex. The precipitate is allowed to agglutinate during 24 hours, at the end of which time it is readily separated as an opaque white lump from the supernatant clear yellow liquid. After being allowed to drain, it is carefully washed twice with a total of 500 cc. of acetone, and the drainings and washings are added to the carbon tetrachloride-acetone solution. The further treatment of this precipitated rubber is described later.

Isolation of the Dissolved Matter.—The carbon tetrachloride-acetone solution is now concentrated to a small bulk by distillation from a steam bath, and the residue is transferred quantitatively to a porcelain basin from which the remaining solvent is allowed to evaporate. The residue, weighing 10–20 grams, is a tacky, semi-fluid mass which varies in color from yellow to deep red in different specimens. It will be referred to for brevity as "the organic-soluble components."

The mixed solvent readily lends itself to the recovery of carbon tetrachloride.

Isolation of the Individual Organic-Soluble Components.—It has been found that this complex mixture of substances not previously isolated from latex is most readily separated into its primary components by selected solvent action. In outline, the method adopted involves extraction of the material first with water and then with rectified spirits. In this way are obtained (*a*) the water extract, (*b*) the alcohol extract, and (*c*) the residue, now to be described. As the detailed chemical examination of the resulting components is not yet complete, only a brief indication of their general nature is now given.

(*a*) *The water extract.* The organic-soluble components from one liter of latex are thoroughly extracted three times at room temperature by vigorous stirring with distilled water totalling 100 cc. On drying the extract to constant weight on the water bath a colorless crystalline residue is obtained, which represents approximately 0.02 per cent by weight of the latex. This sometimes contains a small amount of quebrachitol, but in the main consists of the ammonium salt of a water-soluble aldehydic or ketonic acid. Pending its more complete description it will be referred to as the "ammonium salt."

(*b*) *The alcohol extract.* The material remaining after the water extraction is carefully kneaded five times at room temperature with a total volume of 210 cc. of rectified spirits (3×50 and 2×30 cc.). Evaporation of the combined extracts on the water bath leaves a deep red oil containing more or less crystalline matter and constituting on an average 0.5 per cent by weight of the latex.

This material is now divided into components by treating it three times with petroleum ether (total volume 100 cc.).

(*i*) *The petroleum ether-insoluble portion or "Ester."* This substance is relatively small in amount (approximately 0.05 per cent by weight of the latex), and when first isolated is a crystalline solid white or pale brown in color. Its components are (*a*) a water-soluble aldehydic or ketonic acid and (*b*) a higher aliphatic alcohol. It is thought that the acid may prove to be the same as that occurring in the "ammonium salt" (above), while the alcohol gives evidence of being identical with that isolated from crepe rubber by Bruson, Sebrell, and Vogt[1] and diagnosed by them as octadecyl alcohol. A small amount of quebrachitol is at times associated with this ester, and may be removed in virtue of its insolubility in absolute alcohol.

(*ii*) *The petroleum ether-soluble portion or "Fatty Acid Complex."* This comprises on an average 0.45 per cent by weight of the latex, that is, 90 per cent of the alcohol-extractable material. As first obtained it is a deep red oil and is weighed in this form, but an alcohol solution of the material deposits almost quantitatively a homogeneous crystalline mass. Preliminary work indicates that the eight to ten component substances are isolable from the mixture only after hydrolysis. These facts, together with the mode of isolation of the material, provide the justification for classing it as a single latex component of the type of a "chemical complex" of considerable stability. The preliminary work further shows that the complex consists in the main of fat acids, saturated and unsaturated, which are presumably identical with those isolated from the acetone extract of crepe rubber by Sebrell (*loc. cit.*) and by Whitby, Dolid, and Yorston,[2] and identified by them as oleic, linoleic, and stearic acids. The remaining material is terpenic in character, and it is anticipated that further work will show it to consist of the substances diagnosed, in part by Sebrell and in part by Whitby (*loc. cit.*), as phytosterol, phytosterol glucoside, a hydrocarbon, $C_{15}H_{24}$, a ketone, $C_{15}H_{24}O$, and sterols, $C_{27}H_{42}O_3$ and $C_{20}H_{30}O$.

(*c*) *The residue.* This extremely interesting material, the existence of which

either in latex or in rubber has hitherto been unsuspected, is one of the major non-rubber components. It is widely variable from specimen to specimen in amount, in color, and in texture, but is in general a cream-colored or brown plastic material constituting approximately 1 per cent by weight of the latex. It is weighed after the adhering alcohol has been allowed to evaporate at room temperature. Since its composition and characteristics are still being studied, mention will be made in this preliminary paper only of three observations: first, that the material is freely soluble in ether to a mobile solution; second, that it melts to a viscous liquid below 100° C.; and third, that it holds in combination a sulfur-containing acid. For convenience it will be called the "sulfur complex." It is interesting that a somewhat similar substance results when crepe rubber is allowed to react with thioglycollic acid at room temperature.[3]

NOTE. In preliminary work, the water extraction (above) was followed by an extraction of the residue with dilute aqueous sodium carbonate. As this operation on no occasion gave evidence of removing acidic substances, it was discontinued.

Drying of the Precipitated Rubber.—The acetone-washed mass of precipitated rubber (above), after being allowed to drain thoroughly, is repeatedly passed between cold rolls, the nip being gradually reduced until a thin, pale yellow sheet results. This is allowed to dry in air to constant weight. This product has the interesting property of dissolving almost without swelling in the usual rubber solvents to form opalescent, relatively mobile solutions. An investigation of its physical and mechanical properties is being made.

Removal of Non-Rubber Substances from the Precipitated Rubber.—The dried sheet of precipitated rubber contains the whole of the sugar, quebrachitol,* inorganic matter and protein of the original latex. The following method has been developed for the almost complete removal of these substances in the form of a single water-soluble complex, to be known as the "protein complex."

Ten grams of the precipitated rubber are dissolved in carbon tetrachloride (300 cc.) in a two-liter round-bottomed flask, distilled water (1000 cc.) is added, and the whole is vigorously shaken for some time. The flask is then placed in a water bath until the carbon tetrachloride begins to boil, at which stage a current of steam is passed through the mixture until all the carbon tetrachloride is removed. The resulting aqueous solution and the rubber are now separated as completely as possible (the voluminous rubber phase contains much solution which can be removed by pressure), and the water is removed from the solution until the residue is of constant weight.

The Protein Complex.—The above residue is a pale brown, somewhat hygroscopic syrup with a biscuit-like odor, which slowly crystallizes in air in well-formed elongated plates of considerable size. It is almost completely soluble in a small amount of cold water, and the solution gives the ninhydrin test for protein. Fehling's solution is, however, unaffected owing to the absence of free reducing sugars, while the reactions with ammoniacal silver nitrate and ammonium molybdate are masked by the fact that quebrachitol and the metallic phosphates are also not present as such, but as components of a chemical complex.

All four reagents, however, give normal positive tests if the aqueous solution of the complex is first hydrolyzed by boiling it for half an hour with its own volume of $5 N$ sulfuric acid. Phenylglucosazone (m. p. 203°) has been obtained by suitable treatment of the hydrolyzate.

It may therefore be stated that the components of the complex include protein,

* With the exception of the very small amounts sometimes found with the organic-soluble components.

phosphate, glucose or fructose (or polysaccharides from which they are derivable), and quebrachitol. The observations noted in the ensuing section indicate that this complex also comprises the remaining inorganic components which have been recorded by previous workers. It is anticipated that the material will readily lend itself to the determination of its major components.

Pure Rubber Hydrocarbon.—The rubber remaining after the above water extraction is milled to the thinnest possible sheet in a stream of water, surface water is removed, and the product is then dried to constant weight *in vacuo* over sulfuric acid. This operation is usually complete in 48–72 hours, but on occasion the rubber at this stage is too tacky to be handled quantitatively.

This product consists of rubber hydrocarbon in a highly purified state. It retains a relatively small amount of protein, and when burnt yields only an imponderable residue which is phosphate-free. Other features of the substance including the above-mentioned variability will be discussed in a subsequent paper.

Typical Results

It will be noticed that the total amount of non-rubber components (excluding water) is about 4 per cent of the latex and 10–15 per cent of the latex total solid. These figures are appreciably higher than have been observed hitherto, and are mainly attributable to the inclusion for the first time in a table of this kind of the "sulfur complex," which is seen to be a major non-rubber component.

The percentage of water is obtained from the "Total Solids" determination, which is a routine part of each analysis.

TABLE I

Latex Constituent	Latex A, Per Cent	Latex B, Per Cent	Latex C, Per Cent
Ammonium Salt	0.02	0.03	0.02
Ester	0.06	0.06	0.02
Fat Acid Complex	0.41	0.33	0.47
Sulfur Complex	0.92	0.94	1.16
Protein Complex	2.56	1.45	2.05
Rubber	32.92	27.17	32.98
Water	62.75	69.78	63.68
Total	99.64	99.76	100.38

Additional Considerations

(*i*) In most cases the amount of a given component isolated by the above procedure, though definite, is admittedly small. For the more detailed investigations which are in progress, these small amounts are allowed to accumulate over a period, and are stored in solution in well-stoppered bottles which are kept in darkness.

(*ii*) It will be appreciated that, in dealing with a mixture of this degree of complexity, which shows wide variations in composition from day to day, technical difficulties are encountered from time to time in applying the above method of analysis. All such difficulties to date have been readily dealt with by using ordinary measures, and particulars are therefore omitted from the above account.

(*iii*) Objection may be raised that the above method does not ensure that latex components of high volatility would be observed. This point has been met by subjecting the fresh latex from time to time to distillation with steam. On no occasion has any evidence thus been obtained of the existence in latex of detectable amounts of volatile acids, bases, or aldehydes such as hydrocyanic, hydrosulfuric, formic and butyric acids, ammonia, methylamine, and acetaldehyde, claims for all of which have been put forward in the earlier literature.

Summary

(*i*) A method is described for the quantitative isolation of the chief components of Hevea latex in the form in which they occur in nature.

(*ii*) Several hitherto unknown components have been observed, and receive a preliminary description. They include a sulfur-containing plastic material which is of major importance.

(*iii*) The known major components—sugar, quebrachitol, phosphates, protein, fat acids—are shown to exist in fresh latex, chiefly as components of stable chemical complexes.

(*iv*) It is hoped in the near future to report the results (*a*) of more detailed investigations, and (*b*) of applications of the method in the study of some fundamental problems.

Acknowledgment

Literature Cited

[1] Bruson, Sebrell, and Vogt, *Ind. Eng. Chem.*, **19**, 1187 (1927).

[2] Whitby, Dolid, and Yorston, *J. Chem. Soc.*, **128**, 1448 (1926).

[3] Holmberg, *Ber.*, **65**, 1349 (1932).

Softening and Freezing of Crepe*

T. H. Messenger and J. R. Scott

Introduction

The influence of heat on the mechanical properties of soling crepe has already been mentioned in Part I. The present experiments constitute a fuller examination of this influence and of the effects of storage at low temperatures both before and after heat treatment.

These experiments were made some time ago, and several papers have since appeared dealing with the same or closely related subjects. These will be discussed in relation to the present results.

Experimental

(1) Methods.—Schopper rings from sheets of soling crepe were heated by immersion in water. A preliminary comparison of heating to 100° C. in water and in air showed that these treatments produced the same changes in the rubber, except that prolonged heating in air had a tendency to cause falling off in tensile strength due to oxidation. The changes, especially at first, were slower in air, owing to the lower heat capacity of air.

Water absorption tests (to be described in a later report) indicated that crepe absorbs considerable amounts of water during prolonged immersion, and this absorption must affect the mechanical properties to some extent. For the periods of immersion used in the present experiments, however, this effect was only slight.

Freezing was effected by storing the rings over ice. Tensile tests were made on the Schopper machine, a uniform temperature being maintained in each set of tests in view of the rapid variation of mechanical properties with temperature (see paragraph 6).

(2) Effect of Heat on Gristly Crepe.—An estate-prepared gristly crepe (*i. e.*, a crepe prepared freshly without any heat treatment such as is applied in making golden crepe) was frozen for 33 days, then heated for various periods at 6 different temperatures. Mechanical testing results are given in Table I.

(i) General characteristics of softening. The term *softening* in the present report refers not so much to the property of hardness as to tensile properties. A rubber characterized by low tensile strength and high extensibility will be considered soft or softened, while a rubber characterized by high tensile strength and low extensibility will be considered hard or unsoftened.

The general effect of heating rubber at 70–100° C. is to lower the tensile strength and rigidity (load required to produce a given extension) and to increase the extensibility and permanent set. These changes are initially rapid, but later so slow that approximate constancy is reached, except in the case of permanent set. The continuous increase in permanent set indicates a transition from an essentially elastic condition to a viscous fluid condition.

The tensile strength at first shows a brief rise to a maximum, which corresponds with the first rapid increase in breaking elongation. The subsequent period in which the breaking elongation remains approximately constant corresponds to the

TABLE I

Temp. °C.	Heating Period (Min.)	Tensile Strength (G. per Sq. Mm.)	Breaking Elongation (Percentage)	Rigidity (G. per Sq. Mm.) at 200%	400%	600%	Permanent Set after Rupture (Percentage)
..	0	high	224	..	..	..	3.3
100	0.17	203	413	..	..	..	9.9
	0.5	379	780	43	55	155	22
	1	271	762	42	50	130	22
	2	148	729	38	43	86	35
	5	105	756	35	36	58	41
	10	105	790	33	34	49	51
	30	78	789	33	35	45	48
	100	55	872	28	28	34	64
	240	52	842	..	..	29	71
80	1.25	239	706	42	54	147	..
	3	279	761	41	48	113	..
	10	204	818	40	41	76	..
	30	112	815	34	37	56	..
	100	90	803	33	34	44	..
	240	78	840	32	32	38	..
67	2	214	620	48	74	204	..
	5.5	315	761	45	59	154	..
	15	175	712	40	48	105	..
	46	88	655	38	42	73	..
	120	111	797	35	36	53	..
	240	78	797	33	34	42	..
	360	90	835	33	34	42	..
	525	86	854	34	34	39	..
50	30	208	391	81	..	..	..
	100	221	471	67	158	..	..
	300	229	550	59	119	..	..
	660	256	661	49	82	206	..
	1440	246	601	51	90	245	..
	2880	357	722	49	80	221	..
	6120	357	750	45	65	173	..
40	120	267	304	174	..	..	..
	240	242	278	143	..	..	..
	660	326	282	137	..	..	..
	1440	265	263	168	..	..	..
	2880	357	355	131	..	..	..
	6120	296	328	128	..	..	..
	12000	336	341	131	..	..	..
30	270	302	253	210	..	..	..
	660	315	256	216	..	..	..
	1440	410	278	223	..	..	..
	2880	399	276	232	..	..	..
	6120	357	260	231	..	..	..
	12000	389	257	263	..	..	..

simultaneous decline in breaking load and increase in extensibility. The small final decrease in breaking elongation observed at 100° C. after prolonged heating is more marked in other experiments (see, for example, Table III). It is particularly noticeable in weaker crepes, and may be due to the effects of water absorption referred to above.

The breaking elongation affords the clearest distinction between softened and unsoftened crepes, the former giving 700–800 per cent, while the latter rarely exceed 250 per cent.

(*ii*) *Influence of temperature of softening on changes in tensile properties.* The results in Table I indicate three different effects.

At 67–100° C. complete softening occurs, the time required being longer the lower the temperature. The properties of the completely softened rubber are approximately independent of the temperature used within the range in question. At and below 40° C., on the other hand, true softening, in the sense defined in the preceding section, does not occur. There is a slight decrease in rigidity, a kind of thawing, as it were, at 40° C., but at 30° C. the rubber actually tends to harden.

At 50° C. between these two sets of phenomena the changes resemble the initial phase of softening, *i. e.*, increase in tensile strength and rapid rise in breaking elongation. The large fall in tensile strength characteristic of true softening has not occurred within the time limits of the experiment. There must therefore be an essential change in the effect of heat between 40° and 67° C. and somewhere near 50° C. This is confirmed by the following points observed in Table I.

From the times required to reach a rigidity of 50 g. per sq. mm. at 600 per cent elongation, the results at 67°, 80°, and 100° C. indicate a practically constant temperature coefficient of 2.34 for 10° C. for the rate of softening over this temperature range. If this coefficient were valid for all temperatures, the same rigidity should be attained after 580 min. at 50° C., 1350 min. at 40° C., or 3160 min. at 30° C. Actually, however, softening does not occur even after much longer periods at these temperatures, indicating some fundamental change in the heat effect between 50° and 67° C.

Again, the early maximum in the tensile strength occurs at the following times: 0.5 min. at 100° C.; 3.0 min. at 80° C.; 5.5 min. at 67° C.; 4500.0 min. at 50° C.; indicating once more the essential change in the heat effect.

This discontinuity in the heat effect was observed with all the crepes examined over a temperature range, and in some of these cases true softening was observed at 60° C., so that the discontinuity lies between 50° and 60° C. This observation agrees with the results of many other investigators, who have found the following changes to occur in raw rubber at about this temperature:

(*a*) The plasticity-temperature curve shows a discontinuity between 50° and 60° C.; below 50° C. rubber exhibits considerable elasticity, but above 60° C. it behaves rather as a viscous fluid. (Marzetti.[1])

(*b*) Calender grain shows a sudden decrease at about 65° C. (de Visser.[2])

(*c*) At about 60° C. or above, all residual strains in stretched rubber, however great, are released, that is, 60° C. represents the upper limit of the melting-point range of the rubber crystallites produced by stretching. (Feuchter.[3])

(*d*) Above 60° C. stretched rubber shows no crystal x-ray diagram. (Hauser.[4])

(*e*) The retractive force exerted by stretched raw rubber increases up to 50° C. and then decreases. (Hock.[5])

(*f*) The breaking elongation shows a maximum at 60° C. (Hauser and Rosbaud.[6])

(*g*) The rate of depolymerization of raw rubber by heat increases very rapidly between 60° and 70° C. (Bernstein.[7])

(*h*) Deterioration (tackiness) and fall in solution viscosity do not occur until heating is carried above 50–60° C. (de Vries.[8])

(*i*) Vulcanization takes place only at temperatures above 60° C. (Spence.[9])

(*j*) The rehardening of masticated rubber is much more rapid above 55° C. than below. (Griffiths.[10])

A summary and discussion of the changes at this temperature is given by Stoll.[11]

(*3*) *Effect of Previous Freezing on Softening.*—Earlier work (Part I) indicated

that softening might be influenced by previous freezing of the rubber. Two crepes (No. 41, estate-prepared; No. 43, factory-prepared) were therefore treated as follows: (a) stored at 25° C. for 55 days; (b) stored at 0° C. for 55 days; (c) stored at 0° C. for 55 days and then at 25° C. for 44 days. After storage the crepes were heated at 100° C. for various times to soften them. The results are given in Table II.

Comparison of (a) and (b) shows that the preliminary freezing in (b) does not increase the strength and stiffness of the rubber as might have been expected, but rather tends to produce the opposite changes. Storage at 25° C. after freezing, as in (c), produces unexpected effects also, the strength and stiffness being increased by amounts which more than compensate for the effects of freezing, so that samples (c) are stronger and stiffer than either (a) or (b).

TABLE II

Softening Period (Min.)	Tensile Strength (G. per Sq. Mm.)			Breaking Elongation (Percentage)			Rigidity (G./Mm.)^2 at 600% Elongation		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
Crepe No. 41									
0.5	147	81	181	692	630	791	79	91	95
1	101	84	140	..	730	790	62	62	72
2	82	55	78	800	690	744	51	42	55
5	66	46	62	800	761	735	39	36	45
10	53	42	60	800	748	797	33	31	40
30	38	33	40	729	821	761	32	26	30
100	25	24	26	753	600	756	24	24	26
Crepe No. 43									
0.5	75	82	129	563	512	642	..	..	132
1	63	61	94	625	600	694	61	61	80
2	53	54	63	665	655	642	50	51	66
5	44	36	58	686	660	646	37	34	58
10	39	33	50	682	675	689	38	32	44
30	29	38	43	575	682	709	30	31	34
100	23	22	24	660	547	615	23	..	23

These results have been confirmed by experiments on crepes of various types softened at various temperatures, a summary being given in the following Table III. The term "Factory" refers to sole crepe prepared in this country by remilling ordinary crepe.

In every case previous thawing at 25° C. improves the tensile strength and rigidity of the softened rubber, although the magnitude of the improvement varies greatly from sample to sample and appears to be independent of its origin.

This effect of thawing has been observed by Stevens,[21] who states that "freezing and careful thawing of rubber considerably increase the tensile strength in the unvulcanized condition."

TABLE III

Crepe	Origin	Softening Temperature, °C.	Property	Frozen and Softened (G. per Sq. Mm.)	Frozen, Thawed at 25° C., and Softened (G. per Sq. Mm.)
41	Estate	100		31	40
42	Estate	80	Load	145	188
42	Estate	65	at	165	206
43	Factory	100	650%	32	44
44	Factory	80	Elongation	27	56
44	Factory	65		38	83
33	Estate	100	Breaking	57	113
34	Estate	100	Load	58	120

(4) *Freezing of Previously Heated Crepe.*—(*i*) *Influence of the temperature of heating.* It has been stated that golden crepe (made by pressing ordinary crepe between platens at 100–120° C.) does not harden unless kept cold for a very long time. A golden crepe was therefore included in the following freezing experiments, the samples examined being:

	Tensile Strength (G. per Sq. Mm.)	Breaking Elongation (Percentage)	Rigidity at 200% (G. per Sq. Mm.)
E—Estate gristly	340	195	..
F—Factory gristly	150	188	..
G—Golden crepe	224	598	47

Rings of each were softened by heating (*a*) 20 min. at 100° C.; (*b*) 80 min. at 80° C.; (*c*) 200 min. at 67° C.; (*d*) 4740 min. at 50° C.; and (*e*) 4740 min. at 40° C. They were then stored over ice for various periods, and mechanical tests made immediately after removal from ice. The results are given in Table IV, those for the golden crepe being incomplete owing to lack of material.

The changes occurring during freezing are as follows:

Gristly Crepes: The results for estate and factory samples are broadly similar. Tensile strength increases rapidly during the first 3 days, after which the changes are smaller and irregular, though with the milder heat treatments there is a tendency to decrease on prolonged freezing. The estate crepe often shows a maximum at 3 days.

TABLE IV

Heating Temp., °C.	Freezing Period, Days	Tensile Strength (G. per Sq. Mm.)			Breaking Elongation (Percentage)			Rigidity at 200% Elongation (G. per Sq. Mm.)		
		E	F	G	E	F	G	E	F	G
100	0	470	63	120	875	698	830	42	30	32
	3	540	220	405	795	793	960	41	30	31
	8	470	190	230	582	505	680	65	61	40
	19	440	317	270	666	340	420	128	145	85
	35	330	265	230	369	365	347	134	122	128
	71	420	320	320	473	391	400	99	129	112
80	0	550	72	..	842	744	..	44	29	..
	3	640	200	..	830	723	..	38	32	..
	8	514	270	..	545	500	..	95	79	..
	19	570	280	..	448	380	..	149	130	..
	35	300	230	..	349	333	..	136	137	..
	71	470	350	..	481	405	..	100	114	..
67	0	422	87	275	821	726	940	48	32	36
	3	713	230	360	625	611	911	77	47	31
	8	711	170	360	490	400	720	140	80	45
	19	653	330	400	428	336	430	162	162	119
	35	762	260	470	502	330	438	134	131	133
	71	660	230	530	560	356	585	97	105	95
50	0	320	90	..	513	308	..	103	68	..
	3	550	300	..	374	282	..	225	190	..
	8	575	260	..	396	266	..	223	190	..
	35	500	240	..	368	260	..	213	187	..
	71	470	170	..	440	283	..	147	118	..
40	0	365	130	280	240	278	891	..	104	35
	3	550	310	228	230	255	702	485	230	39
	8	580	270	370	228	224	514	509	240	80
	35	530	290	..	240	241	..	420	250	..
	71	480	250	470	241	261	480	380	200	100

Rigidity increases to a maximum and then slowly decreases. This decrease, and the corresponding tensile strength decrease, agree with the previous observation (paragraph 3) that prolonged freezing lowers tensile strength and stiffness. Incompletely softened samples (40° and 50° C.) attain maximum rigidity rapidly (5–10 days), but complete softening (at 67°, 80°, or 100° C.) delays this maximum to about 20 days. The rigidity throughout the freezing period is higher the lower the original heating temperature, though this difference is much smaller over the range 67–100° C. than over the range 40–67° C.

In the completely softened samples, the breaking elongation, after a brief tendency to rise, falls rapidly, reaching a minimum in about 20 days, and finally tends to increase; these results are what would be expected from the changes in tensile strength and rigidity. The 40° and 50° C. samples, being incompletely softened at the beginning, naturally show a much smaller decrease during freezing.

Golden Crepe: This behaves in much the same way as the gristly crepe, but the rigidity maximum and breaking elongation minimum are delayed to 30–40 days. The fact that even the incompletely softened (40° C.) golden crepe samples behave during freezing like softened gristly crepe is due to the golden crepe having been softened during manufacture, this softening being not permanently reversible by freezing (see paragraph 5).

No essential difference between the freezing of golden and gristly crepes is apparent, therefore, though golden crepe freezes rather more slowly. Comparison of the rigidity figures for frozen samples with those for the original material shows that golden crepe hardens considerably when stored at 0° C., so that the statement that golden crepe does not harden is incorrect; other experiments (paragraph 5) show, however, that this hardening is only temporary.

(*ii*) *Influence of period of heating.* The period of softening influences the rate of subsequent freezing, as is shown by the following figures:

TABLE V

Softening Period, at 100° C.	Tensile Strength (G. per Sq. Mm.) Immediately after Softening	After 7 Days at 0° C.
0.5 min.	379	546
2 "	148	504
30 "	78	302

The rate of recovery during freezing clearly shows a maximum for a particular softening period, shorter periods giving a lower rate because softening is incomplete, while longer periods slow down the recovery by producing a more deep-seated change in the rubber.

(5) *Effect of Softening, Freezing, and Resoftening.*—An estate crepe was softened by heating for 420 min. at 67° C., kept at 0° C. for 108 days, then resoftened at 67° C. The changes occurring during the two softening periods are shown in Table VI.

Freezing only partially reverses the changes produced by the first softening, and the recovery on freezing is only temporary, being completely eliminated by 2 min. heating at 67° C., whereas in the first instance 400 min. were required for complete softening. The second softening, after the first 2 min., merely continues the changes produced by the first softening, as though no intermediate freezing has occurred.

Precisely similar results were given by a factory-prepared crepe.

It is possible that the very rapid fall in rigidity observed in the second heating occurs also during the first heating, as the general form of the softening curve for

temperatures above 60° C. (see results in Table I) suggests the superposition of two changes, one practically complete in 2 or 3 minutes, and the other much slower, continuing for some hours.

Kröger[15] examined the effect of heat on raw rubber which had apparently been masticated (though this is not definitely stated) and allowed to harden by storage for some years; this treatment corresponds approximately to the first softening and freezing in the present experiments. Heating for 1 minute at 34° C. and above produced complete softening, but temperatures below 30° C. had little effect.

TABLE VI

	Softening Period (Min.)	Tensile Strength (G. per Sq. Mm.)	Breaking Elongation (Percentage)	Rigidity (G. per Sq. Mm.) at	
				400%	600%
1st Softening	0	259	171	..	..
	2	220	553	119	..
	10	235	583	112	..
	30	220	652	87	..
	100	171	644	67	140
	200	175	707	53	120
	420	155	756	42	97
2nd Softening	0	333	443	270	..
	2	129	706	46	80
	10	125	724	45	76
	30	99	677	44	76
	100	115	747	41	75
	200	106	762	37	60
	420	88	751	35	54

It appears, therefore, that crepe once softened by heating above 60° C. cannot be restored to its original gristly condition by cold storage within a reasonable period of time. The temporary hardening which occurs on cold storage is rapidly eliminated by heating above 34° C.

(6) *Influence of Temperature on Tensile Testing of Crepe.*—In view of the enormous change in mechanical properties produced by heat, it seemed obvious that testing temperature must considerably influence the results obtained in tensile tests. Experiments were therefore made at 12°, 21°, and 30° C., using thin crepe to facilitate temperature equilibrium. Tests were made on rings softened for 5 min. at 100° C. and on untreated rings, both sets being maintained at the testing temperature for 30 min. before being broken.

As the tensile strength, tensile product, and rigidity all decrease rapidly with rising testing temperature, it is clear that comparable results in tensile tests on crepes will be obtained only under conditions of uniform temperature. The same conclusion is reached by Hauser and Rosbaud,[6] Le Blanc and Kröger,[16] and Feuchter.[17] Hauser and Rosbaud[6] and Feuchter[18] show also that the rate of elongation considerably affects the tensile test results.

TABLE VII

	Temp., ° C.	Tensile Strength (G. per Sq. Mm.)	Breaking Elongation (Percentage)	Rigidity (G. per Sq. Mm.) at:		Tensile Product
				100%	600%	
Untreated	12	492	146	339	..	121
	21	254	148	191	..	64
	30	137	184	81	..	38
Softened	12	190	681	29	130	148
	21	100	679	27	85	78
	30	65	699	24	51	52

Some further experiments were made with a view to determining suitable conditions for the measurement of permanent set after rupture. Rings were softened for 5 min. at 100° C., hardened somewhat by freezing at 0° C. for 7 days, and then broken. The broken rings were kept at various temperatures and the set measured periodically.

TABLE VIII

Time after Breaking (Min.)	Percentage Permanent Set after Rupture after Storage at:			
	20° C.	25° C.	34° C.	70° C.
0	154	142	136	142
7	145	34.7	22.1	12.8
15	143	29.6	16.8	10.8
42	143	27.7	15.1	8.6
135	143	24.7	13.2	8.2
490	143	23.7	10.5	7.3
After further heating to 100° C. for 1 min.	10.5	7.9	7.2	6.0

After about 2 hours, whatever the temperature, the permanent set reaches an approximately constant value which is smaller the higher the temperature. The high set at low temperatures is largely eliminated by brief heating at 100° C., and longer heating at this temperature would probably equalize the set of all the samples. In carrying out permanent set tests, therefore, it will be advisable to make measurements after storage at some convenient low temperature (15–20° C.) and again after a standard period of softening at 100° C.

The sudden fall in the residual set between 20° C. and 25° C. observed in Table VIII agrees with the observations of Hock[5] and Feuchter.[3, 12, 13,14] Both these authors find that raw rubber when stretched and kept at a low temperature retains a very high permanent elongation, which is partially released on warming to a critical temperature given by Hock as 21–24° C. and by Feuchter as 20° C. Feuchter noted also that the residual set after heating was less the higher the temperature. It is to be noted that in the experiments above the rubber had been permanently softened at 100° C. before rupture, whereas Hock and Feuchter used untreated raw rubber. Evidently the softening does not affect the critical temperature of 20° C. at which set is released.

Summary and Conclusions

The outstanding results may be summarized as follows:

(*i*) Heating gristly crepe to 60° C. or above causes softening, a change characterized by a large fall in tensile strength and rigidity and by increase in breaking elongation and permanent set. With some crepes there is a transient initial rise in tensile strength. Subsequent storage at 0° C. produces changes in the reverse direction, which, however, are rapidly eliminated by heating at 34° C. or above. It appears, therefore, that heating above 60° C. produces: (*a*) a permanent change not reversible by freezing; and (*b*) a temporary change reversible by freezing.

(*ii*) Heating gristly crepe below 50° C. only moderately increases the extensibility and flexibility, true softening being absent. These changes are reversible by freezing, the recovery being quicker than with softened crepe.

(*iii*) Prolonged storage at 0° C. (beyond 20–30 days) causes a gradual decrease in strength and stiffness in both gristly and softened crepes. With gristly crepe

these effects are more than counteracted by thawing at 25° C., giving a tougher, stronger product than the original.

(*iv*) The statement that golden crepe does not harden is incorrect; as, however, this is a softened crepe the hardening is only temporary and does not restore the original gristly qualities.

(*v*) Uniform temperature and rate of elongation are essential in tensile tests on raw rubber. The permanent set of broken rings becomes sensibly constant in 2 hours.

From the present results and those of other investigators, it appears that there are 4 temperatures at which fundamental structural changes occur in raw rubber:

(*a*) −58° to −55° C. Below this temperature raw rubber is brittle (Kohman and Peek[25]).

(*b*) 20° to 25° C. Above this temperature the capacity for retaining a large permanent elongation rapidly diminishes. According to Feuchter[3] this is due to 20° C. being the lower limit of the melting-point range of the rubber crystallites produced on stretching, whereas Hock[5] considers that at 20° C. the molecular kinetic energy becomes just sufficient to overcome the cohesion between the parallel elongated molecules. No reference has been found to changes in unstretched rubber at this temperature.

(*c*) 30° to 35° C. The crystalline rubber present in the unstretched material melts at this temperature, causing a sudden decrease in specific gravity and hardness and an increase in transparency (Katz;[19] van Rossem[20]), and, with rubber previously softened above 60° C. and then frozen, a large fall in tensile strength and increase in extensibility. Gristly crepe does not show the latter changes, but whether it shows the other changes mentioned is not clear, as the pre-treatment (if any) of the rubber samples used is not stated.

(*d*) 50° to 60° C. Above this temperature raw rubber loses the power to acquire a crystalline structure on stretching, and its mechanical properties change from those of an essentially elastic body to those of a more or less fluid or plastic body;* this loss of elasticity must result partly from the inability to crystallize, since elasticity is a characteristic of crystals. Rapid depolymerization and the ability to react with sulfur begin at 60° C., the one presumably resulting from the other. As depolymerization is a chemical process, probably non-reversible, this may possibly be the non-reversible change referred in paragraph (*i*) on page 14; alternatively, this change might represent the breaking down of a structure produced by the agglomeration of the cell-like latex particles. The reversible change referred to might, in view of the two-phase structure assigned to rubber (see, *e. g.*, Hauser[22]), be regarded as a transition to a single phase, the two phases being completely miscible above 60° C.; this change would cause a transition from elastic towards fluid behavior, as actually observed, and would also account for the tendency, noticed in the present experiments, for the properties of rubber to be more sensitive to temperatures below 60° C. than above.

Reverting to the question of tensile testing methods for crepe soling, and the relative merits of gristly and golden crepes, it must first be noted that in use a crepe sole quickly undergoes a certain softening, and the real criterion of a sole is therefore the nature of the softened material. If, as seems probable, this softening does not involve the permanent change occurring above 60° C., the original plan (Part I) of heating tensile test-pieces for 5 min. at 100° C. is unsatisfactory,

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* Raw rubber does not, however, behave as a perfectly viscous or fluid material even at temperatures as high as 90° C. (R.A.B.R.M. unpublished experiments; see also van Rossem and van der Meyden.[24]

as it introduces a change not found in actual use; for the same reason a gristly sole will always be tougher and less liable to spread than a golden sole, since it is probable that the temporary hardening of golden crepe is soon eliminated by use. Until the nature of the mechanical softening during use is understood a standard softening procedure for tensile testing cannot be formulated, and a decision as to the relative merits of gristly and golden crepes must likewise be withheld. A softening temperature of 35–45° C. might be suggested tentatively as safer than temperatures above 60° C.

In the test for spreading devised by Stevens,[23] the temperature used (50° C.) seems rather too high, as it borders upon the region of permanent physical change.

In view of the radical changes produced by heating above 50–60° C., the selection and pre-treatment (e. g., mastication) of raw rubber samples to be used in investigations on structure and physical properties, and their exact description in published papers, are matters of great importance, especially as some varieties of raw rubber are subjected to heat during preparation, e. g., Para, smoked sheet (the temperature of the smoke houses ranges from 40° to 55° C., and so may just exceed the softening temperature). The influence of small amounts of foreign substances, e. g., acids or alkalies, on the rehardening of rubber after heating or mastication is a further point to be watched; for instance, a masticated rubber which remains soft on keeping may become hard and rigid if sublimed sulfur is added. This cannot be attributed to vulcanization, as the hardened material is quite unlike vulcanized rubber; it appears rather to be due to traces of acid in the sulfur.

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Specific Properties of Artificial [Buna] Rubber

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Developments in the Synthesis of Rubber

Because of the peculiar properties of natural rubber, its usefulness is somewhat limited, and in many fields of application it is quite unsuitable. In contact with oils and fats it swells rapidly and loses almost completely its good mechanical properties, and besides this natural rubber has poor resistance to heat. Again it is attacked rather easily by oxygen, and on exposure to oxygen and light simultaneously there is a particularly strong tendency to develop cracks within a short time. It is for such reasons that the chemical industries of various countries have been looking for an artificial or synthetic product which is free from the shortcomings of natural rubber or exhibits them to only a relatively small extent.

Experimentation on artificial rubber has depended fundamentally on the discovery of Harries[1] that the natural rubber molecule is constructed of isoprene units. Isoprene and its allied hydrocarbons were prepared by Hoffmann and his coworkers[2] at the Elberfeld dye works, and these compounds were in turn polymerized to masses similar to rubber. These experiments were carried out before the World War. Because of a shortage of raw materials during the War, it was necessary to adapt the laboratory results to a factory scale sooner than should logically have been done. At that time the most readily available technical raw material was dimethylbutadiene, a compound which differs from isoprene by the presence of an extra methyl group, as may be seen in Table I.

TABLE I

FUNDAMENTAL HYDROCARBONS OF ARTIFICIAL RUBBER

Compound	Formula	Constitution	Classification
Butadiene	C_6H_4	$H_2C{:}CH.CH{:}CH_2$	Gas, b. p. $-4°$ C.
Isoprene	C_5H_8	$H_2C{:}CCH_3.CH{:}CH_2$	Liquid, b. p. 33° C.
Dimethylbutadiene	C_6H_{10}	$H_2C{:}CCH_3.CCH_3{:}CH_2$	Liquid, b. p. 69° C.

So-called methyl rubber was prepared from dimethylbutadiene. It was well adapted to the manufacture of hard rubber, but in the soft rubber field it left much to be desired in elasticity and resistance to tearing. Since sufficient natural rubber was again imported into Germany after the War, work on the preparation of methyl rubber was suspended. During the War about 2500 tons of methyl rubber were manufactured in Germany.

In 1926 technically satisfactory methods were developed for the manufacture of butadiene, and, as a result of this, experimentation on artificial rubber at the I. G. Farbenindustrie A.-G. was resumed. The success of these investigations is evident by the appearance on the market of so-called "Buna" artificial rubbers. Buna rubber is free from the shortcomings of methyl rubber, and the properties of its vulcanizates closely resemble those of natural rubber; indeed, in many respects they are superior.

The raw materials for the synthesis are merely coke and lime, from which calcium carbide is prepared, and, from this, acetylene by the action of water. It is possible in various ways to prepare from acetylene the fundamental unit of Buna rubber, butadiene. Thus acetylene can be converted into acetaldehyde, this in turn into acetaldol, and the latter into butyleneglycol. By removal of two molecules of water, butyleneglycol is transformed into butadiene.

At room temperature, butadiene is a gas which is easily condensed into a liquid. The polymerization of butadiene to synthetic rubber can be accomplished by various methods, but the properties of the final product vary with the method of polymerization.

At the present time the types which are being prepared include Buna N, Buna S, Buna 85, and Buna 115, as may be seen in Table II.

TABLE II

```
                                                      Buna N
                   polymerization in emulsion      ↗
                              ↗                    ↘
Butadiene      ↗                                      Buna S
              ↘                                      Buna 85
                   polymerization with sodium      ↗
                                                   ↘
                                                      Buna 115
```
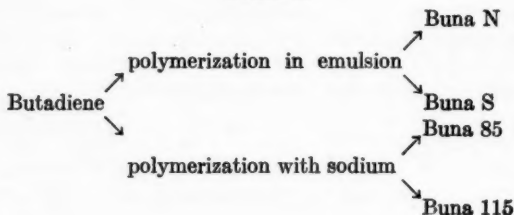
Various Types of Rubber

Buna N and Buna S are emulsion polymerizates. Butadiene liquefied under pressure is finely dispersed in an aqueous emulsifying solution and polymerized in the form of an emulsion. Buna 85 and Buna 115 are polymerized directly as liquid hydrocarbons by means of sodium. The preparation of the various types has passed successfully through the laboratory stage, and is now being carried out on a plant scale. The quantity of synthetic rubber prepared up to the present time is, in terms of the total amount of all rubber needed in Germany, still of no great significance, but with no further developments this quantity can be increased. Admittedly the cost of Buna rubber at the present time still exceeds the market price of natural rubber, but it is certain that when continuous production on a large scale is established, the price of Buna rubber will be reduced.

Processing and General Properties

The processes used in the manufacture of artificial rubber parallel in all essential ways those used for natural rubber. In the processing of Buna rubber mixtures in the unvulcanized state, and in vulcanizing operations, the same machines and equipment are used as in the manufacture of ordinary rubber goods. For vulcanization with sulfur, accelerators[3] and ordinarily zinc oxide as well are necessary. Active fillers, e. g., gas black and active zinc oxide, greatly improve the mechanical properties of artificial rubber.

The harder the polymerized rubber, the more difficult it is to process. Vulcanizates made from the harder types of Buna rubber have, on the other hand, most valuable physical properties. In this respect Buna 85 and 115 differ from Buna N and S. With a degree of polymerization, which is represented by the numeral following "Buna," Buna 85 and Buna 115 are plastic and relatively easily processed, but their physical properties are poorer than those of the harder Buna

N and Buna S.   Unlike natural rubber, Buna N and Buna S can be masticated only to a slight extent, *i. e.*, they are not converted into a soft plastic mass by prolonged milling.   To facilitate processing on a plant scale, softening agents are added to Buna N and Buna S.   Contrary to their effects in natural rubber, these softeners do not have any marked influence on the physical properties of vulcanizates.

Table III shows that the tensile strength of artificial rubber exceeds in some cases that of natural rubber.   It is to be noted further that, since the War, considerable improvement has been made in the old methyl rubber.   The data in Table III were obtained in all cases from mixtures containing active gas black.   Vulcanizates of Buna rubber without active fillers have consistently lower tensile strengths, in fact lower than the tensile strength of natural rubber.

The resistance to cold of the several types of Buna rubber, especially Type N, is somewhat less than that of natural rubber.

TABLE III

PHYSICAL PROPERTIES OF MIXTURES OF ARTIFICIAL RUBBER AND OF NATURAL RUBBER WITH GAS BLACK

	Tensile Strength (Kg. per Sq. Cm.)	Elongation at Break (Percentage)	Stress at 300% Elongation (Kg. per Sq. Cm.)	Shore Hardness	Elasticity (Pendulum Beam)
Natural rubber	260	600	70	65	50
Buna N	300	600	90	70	45
Buna S	275	650	80	65	50
Buna 115	200	700	55	60	40
Buna 85	175	600	50	65	30
Methyl rubber W	125	500	50	Plastic	10

Specific Properties

Artificial rubber has other properties which natural rubber lacks, and these properties give Buna rubber in many respects a preëminent position over natural rubber.   The specific properties of the individual types of Buna rubber show fundamental differences.

For example, only Buna N is resistant to oils and benzine; Buna S, Buna 85, and Buna 115 behave in the same way as natural rubber in organic swelling agents.

The best resistance to abrasion is found with Buna N, followed by Buna S, and then the more highly polymerized Buna 115.   All show decidedly better resistance to abrasion than do natural rubber mixtures.   The lower molecular Buna 85 shows about the same resistance to abrasion as does natural rubber.

Buna S is more resistant to heat than is natural rubber, while Buna 115, Buna 85, and Buna N are about the same as natural rubber in this respect.   Mixtures of these latter types with certain ingredients are more resistant to heat than is natural rubber.

Buna 85 is especially adapted to the manufacture of hard rubber, and its vulcanizates are characterized by high softening points and extraordinary resistance to swelling compared with the behavior of hard rubber prepared from the natural material.

The electrical properties, *e. g.*, the dielectric constants and power factor, are, in the case of Buna 85 and Buna 115, superior to those of natural rubber.   The electrical properties of the oil-resistant type, Buna N, are poorer.

The aging properties of all types of Buna rubber are considerably better than those of natural rubber.

Resistance to Oils

If so-called oil-resistant vulcanizates of natural rubber are brought into contact with organic swelling agents, they frequently swell within a short time to several times their original volumes, and lose almost completely their tensile strength, resistance to abrasion, and structural characteristics. Buna rubber behaves entirely differently, and Buna N in particular swells only slightly in mineral oils, benzine, fats, and vegetable oils. The increase in volume amounts to only a few hundredths. The very small proportion of swelling agent which is absorbed has almost no influence on the mechanical properties; in fact slightly swollen Buna
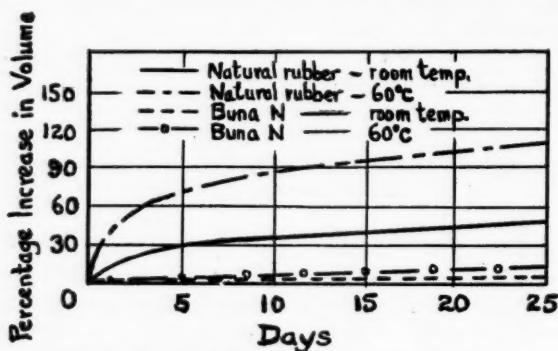

Figure 1—Gain in Weight (Percentage by Volume) of Buna Rubber and Natural Rubber after Immersion in Mineral Oil
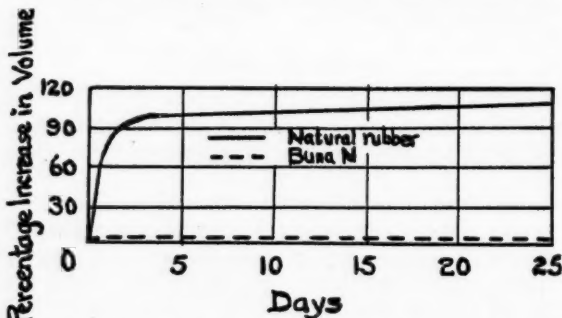

Figure 2—Gain in Weight (Percentage by Volume) of Buna Rubber and Natural Rubber after Immersion in Benzine

vulcanizates even show improved elastic properties. Figures 1 and 2 show these phenomena.

Buna N swells in aromatic hydrocarbons such as benzene, toluene, etc., and in chlorinated hydrocarbons such as carbon tetrachloride, trichloroethylene, etc. In organic solvents of these types Buna N vulcanizates have little adaptability, but fortunately these solvents are of relatively little interest in engineering problems. In mixtures of benzine and benzene the resistance to swelling of Buna N vulcanizates is not so great as in pure aliphatic hydrocarbons, such as mineral oil and benzine. However, for motor fuels like benzine-benzene (6:4) mixtures, Buna N vulcanizates are quite satisfactory, and are far superior to natural rubber vulcanizates, as is evident in Figs. 3 and 4.

Resistance to Heat

At elevated temperatures natural rubber has only limited stability, and even "heat-resistant" rubber mixtures formulated according to the latest experience can hardly be considered as stable over long periods at temperatures above 80° or 90° C. Temperatures above 100° C. or certainly above 150° C. decompose natural rubber quickly. Buna vulcanizates are considerably more stable, but the individual types differ among themselves. Buna S is more resistant to heat than natural rubber, and Buna S vulcanizates which have been exposed for long periods to temperatures above 100° C. show no softening as do natural rubber vulcanizates, but rather undergo a stiffening or hardening. In this respect Buna 85, Buna 115, and Buna N are somewhat inferior to Buna S, but with the proper choice of compounding ingredients it is possible even with these three types to obtain vulcanizates which are superior to those of natural rubber. Experiments on the behavior of Buna at higher temperatures are still incomplete.

Table IV shows the changes in elasticity and hardness of synthetic and natural rubber. Tensile strength values are omitted, because they do not show the characteristic changes as well as do hardness and elasticity values.

TABLE IV

RESISTANCE TO HEAT

(SAMPLES HEATED IN STEAM AT 151° C.)

Hardness (Shore)

	Natural Rubber	Buna
Not heated	60	55
Heated 7 days	43	55
Heated 16 days	33	56
Heated 32 days	25	60

Elasticity (Pendulum)

	Natural Rubber	Buna
Not heated	65	45
Heated 7 days	48	48
Heated 16 days	43	49
Heated 32 days	40	51

Buna S is also superior to natural rubber on exposure to hot air. When heated for only a few hours in air at 150° C. natural rubber vulcanizates acquire a leathery surface, whereas Buna S vulcanizates are still in good condition and quite serviceable, even after having been heated for several days at 150° C.

Resistance to Abrasion

Natural rubber vulcanizates which contain active carbon black as their chief ingredient are several times as resistant to abrasion as steel. A modern tire is a good example of this superiority. Buna rubber is more resistant to abrasion than natural rubber. The several types of Buna rubber show in this respect considerable differences among themselves. Buna N is the most resistant to wear, followed in order by Buna S, Buna 115, and Buna 85. If the abrasive loss of a high grade tire tread is represented by 100, then the relative loss of Buna N is approximately 60, of Buna S 75–80, of Buna 115 approximately 90, and of Buna 85 around 100. In other words, it is possible to prepare Buna N mixtures which under the most favorable conditions wear away only about one-half as rapidly as do the highest grade of tire treads yet made from natural rubber. These values are characteristic of mixtures not softened to any significant extent. Softening agents, which as already mentioned, must be added to the harder types of Buna (N and S) for processing on a

plant scale, lower the resistance to abrasion somewhat. This loss in resistance to abrasion can nevertheless be tolerated, for even under these conditions it is still possible without difficulty to prepare technical products which exceed by approximately 30 per cent the resistance to abrasion of the best natural rubber mixtures. In special cases, where a greater expenditure of work in the preparation and processing of Buna rubber mixtures is acceptable, it is advantageous to choose mixtures containing relatively little softener.

The constitutionally softer Buna 85 and Buna 115 can, as already mentioned, be processed more easily, and require hardly any softening agents for technical proce sing. With these types, softening agents have a very deleterious effect on resistance to abrasion.
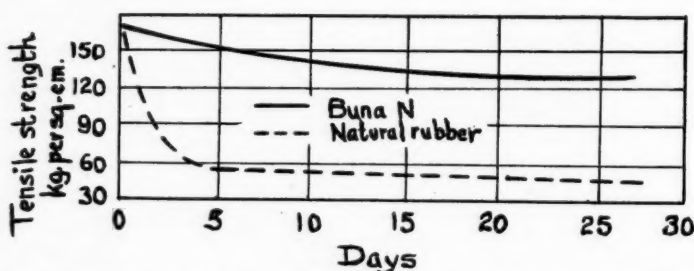
Figure 3—Changes in Tensile Strength of Buna Rubber and Natural Rubber by Immersion in Benzine at Room Temperature
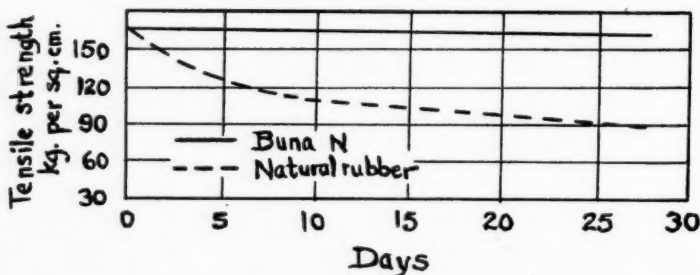
Figure 4—Changes in Tensile Strength of Buna Rubber and Natural Rubber by Immersion in Mineral Oil at Room Temperature

This information on the resistance to abrasion of Buna rubber has been obtained from driving tests of Buna rubber tires which were driven on the Nürburg circuit by the military forces, the experiments being carried on with a fleet of forty cars at one time. The results of laboratory tests are shown in Fig. 5. In these tests the loss by abrasion on a disc covered with emery paper, and rotating eccentrically, was measured. The tests were carried out under various loads, and were confirmed by road tests.

Higher loads on the test specimens changed the relative values shown in Fig. 5 in favor of natural rubber, except for Buna N, the resistance of which was not so dependent on the load. Increased temperatures, i. e., temperature differences which occur in winter and summer in Germany, also have an influence on resistance to abrasion. For example, in cool weather the relative losses of natural rubber and Buna S by abrasion are 100:75 whereas in hot summer weather this ratio be-

comes 100:50, *i. e.*, more favorable to Buna S.   When tires made from natural rubber are driven on wet roads, it has been proved that the loss by wear is slower than it is on dry roads.   In the case of synthetic rubber tires no such differences have been found, for the gripping power of Buna rubber tires is not impaired by softening agents is greater.

Aging

To obtain in the laboratory an insight into the behavior of vulcanized Buna rubber during storage, two artificial aging tests were employed, the Bierer-Davis aging test and the Geer aging test.   In both tests, all types of Buna showed relatively little deterioration in their important physical properties, and that it may safely be
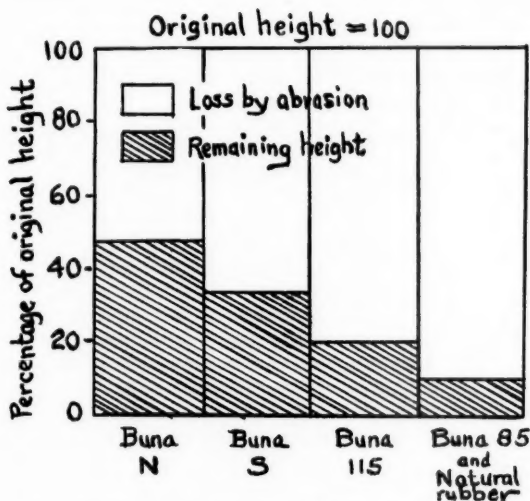

Figure 5—Losses by Abrasion of Buna Rubbers and of Natural Rubber under Similar Conditions

TABLE V

AGING OF RUBBER-CARBON BLACK MIXTURES

Bierer-Davis Method

(Oxygen at 60° C. under 21 Atmospheres' Pressure)

The successive values represent tensile strength (kg. per sq. cm.), elongation at break (percentage) and stress at 300% elongation (kg. per sq. cm.)

	Before Aging	8 Days	16 Days	32 Days
Natural rubber	260–600–60	100–350–55	70–300–45	50–200–45
Buna N	280–650–70	270–650–70	270–600–80	250–600–100
Buna S	260–600–60	250–600–80	240–600–90	230–600–100
Buna 115	205–700–60	200–700–60	190–675–70	180–650–80
Buna 85	170–650–50	165–650–55	160–625–60	150–620–70

Geer Method

(Current of Air at 70° C.)

	Before Aging	8 Days	16 Days	32 Days
Natural rubber	260–600–60	245–530–90	210–500–95	160–350–95
Buna N	290–560–90	280–530–100	280–450–130	. . . .
Buna S	270–675–55	250–650–52	240–600–52	225–575–65
Buna 115	200–750–55	190–725–55	180–650–60	170–625–65
Buna 85	175–700–50	170–675–52	165–650–55	155–600–65

assumed that the high stability of Buna rubbers in both of these artificial tests is true of natural aging. The results of the aging tests are shown in Table V.

Permeability to Gases

As is well known, natural rubber is not completely impervious to gases. This permeability is especially manifest with hydrogen and carbon dioxide. Buna S, Buna 85, and Buna 115 have approximately the same permeability as natural rubber, but Buna N vulcanizates show less than one-half the permeability to air of natural rubber. Experiments on this subject are still incomplete.
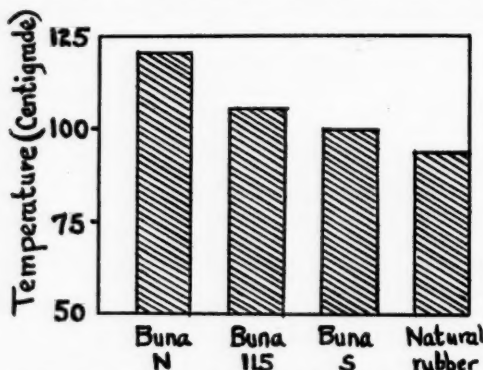

Figure 6—Softening Points of Buna Hard Rubbers
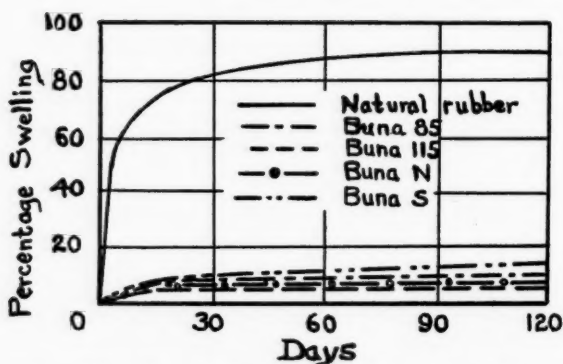and of Natural Hard Rubber on Heating

Figure 7—Swelling of Buna Hard Rubbers and of Natural
Hard Rubber by Immersion in Nitrobenzene

Hard Rubber

A mixture of natural rubber and 1 to 10 per cent of sulfur gives soft rubber vulcanizates. With 30 to 45 per cent of sulfur, hard rubber is obtained. Hard rubber is characterized by good electrical properties, and is stable to acids, alkalies, and salt solutions. This stability to chemicals makes hard rubber an advantageous material to the chemical industry for lining parts of equipment and containers.

Like natural rubber, the several types of Buna rubber can with high percentages of sulfur be vulcanized to hard rubber. Buna 115 and Buna 85 are particularly

suitable for hard rubber, but Buna S and Buna N are also adaptable.   The physical properties of Buna hard rubber are, generally speaking, the same as those of hard rubber prepared from natural rubber.   With respect to resistance to heat, tendency to swell in liquids and resistance to chemicals, Buna hard rubber has certain advantages over hard rubber made from natural rubber.   The resistance to heat is greatly superior, as is evident in Fig. 6.   Toward swelling agents it is less sensitive. With the aid of Buna rubber it is possible to prepare hard rubber linings which give satisfactory service even in contact with nitrobenzene, as can be seen in Fig. 7. Concentrated acids attack Buna hard rubber considerably less than they do ordinary hard rubber.   Buna hard rubber has, on the other hand, the disadvantage of being more brittle than natural hard rubber, a shortcoming which in many cases is especially undesirable in the technical lining of containers of large capacity.

Resistance to Ozone

Natural rubber is attacked with extraordinary rapidity by ozone.   This oxidative destruction of the rubber molecule has been utilized by Harries for explaining the constitution of rubber.   The span of life of vulcanized rubber in the presence of traces of ozone is therefore very short.   In tests of the comparative resistance of natural rubber and Buna N rubber in air containing a little ozone, a natural rubber vulcanizate showed cracks after about 3 minutes, while a Buna N vulcanizate exhibited cracks only after 7 minutes of exposure.

Fields of Application

The peculiar properties of Buna rubber which have been described in the foregoing sections make its possible applications greater than those of natural rubber. In the following section the applications which have been found up to the present time will be described, and other possible places where Buna rubber can be used advantageously and economically as a new construction material will be pointed out.

Resistance to Oils

Up to the present time an oil-resistant, really elastic construction material has been lacking.   The engineer will fully appreciate the importance of having such a material available and the various ways in which it can be used to advantage.

Oil-resistant, thick, treated-fabric packing, thin packing, and gaskets are used where oil-resistance combined with a certain degree of elasticity in the construction is required.   In automobile and machine construction, rubber products made of Buna N rubber are being used more and more for packing rings, gaskets, etc.   Likewise Buna N has proved itself very good as a packing for transformer boxes.

Oil-resistant printing rolls, printing plates, and printing cloth, lacquered and impregnating rolls used in the printing industry and in allied industries are of considerable concern.   The earlier and still commonly used glue-gelatin rolls can be replaced to advantage by Buna N rolls, since the latter are considerably more resistant to abrasion and to cutting.   Because of this, Buna rolls last considerably longer than the earlier type.   Oil-resistant rolls have in the last year been supplied in large numbers by the rubber industry.

Oil-resistant rubber is likewise being used in increasing quantities for hose. The petroleum industry requires hose resistant to benzine and to oils, as does that part of the chemical industry (oil mills, etc.) which processes materials that swell rubber.   To an increasingly great extent hose manufactured with Buna rubber is being tested, for it has the advantages over ordinary metal hose of greater flexibility, greater rate of flow for a given size, and greater ease of cleaning.   Oil-resistant hose for the liquids used in drilling tools is in demand.

Buna N is also well adapted to hose for conducting propane and butane, and for spraying paint, where liquids with a tendency to swell rubber are in contact with the tube.

For studying the effect of lubricating oils, Buna N has been used experimentally as an elastic tube for conducting hot oil. Oil-resistant hose is also used for conducting other liquids. Oil-resistant rubber tubing is always preferable to rigid metal connections where either sharp bending or vibration occurs, both of which impose special demands on the hose in so far as its elasticity is concerned.

In operations involving an explosion hazard, oil-resistant and electrically conducting hose tubes prevent electrostatic charges during the discharge of benzine, etc., and thus obviate the danger of conflagration.

Oil-resistant buffers and supports for machine installations will be of service as dampeners of vibration, where natural rubber is now a failure because of its sensitivity to oil. Here completely oil-resistant Buna N rubber has a wide and still unforseen field of usefulness. The elastic properties of synthetic rubber under these conditions have been investigated in a particularly exhaustive fashion.

Oil-resistant rubber has obtained a foothold in the cable and electrical industries. Because of its resistance to oils, Buna N has great advantages over natural rubber-fabric combinations for sealing the ends of oil-impregnated high-tension cables. There are also cables for hand lamps and electric tools, which in workshops frequently come in contact with oils and thereby become damaged prematurely.

For oil pumps and other equipment for conducting oil, artificial rubber has proved very satisfactory in America as a material to resist swelling, and in that country pump pistons and packing of artificial rubber are being used in increasingly great quantities. Centrifugal pumps with a rubber body in eccentric position have been developed by a German firm. Made of oil-resistant Buna N rubber, this structure makes it possible for the pumps to be used for oils and drilling liquids.

The conveyance of materials containing oil is not practicable with conveyor belts made with natural rubber. The resistance to abrasion of the rubber cover is so diminished by the swelling agent that the cover wears away badly within a short time. A conveyor belt made with Buna rubber does not have this shortcoming.

Oil-resistant V-belts are of considerable importance in machine design, and already in various countries they have made great headway as a driving mechanism. One advantage worthy of note is the fact that, because of the elastic power transmission, chatter marks do not appear on the metal being machined. Oil-resistant V-belts are of great importance in machine tool manufacture, since the drive can be made downward. The manufacture of oil-resistant V-belts from Buna N rubber is now under way, and it is to be hoped that the experimental stage will soon be passed.

Heat Resistance

The superior resistance of Buna rubber compared with natural rubber at elevated temperatures opens to Buna rubber a wider field of application than to natural rubber.

Railway steam hose has been made of artificial rubber in an experimental way. As a result of recently acquired knowledge of mixing technic, there is good reason for hoping that hose made of Buna rubber will give at least as good service as hose made of natural rubber. This applies quite generally to hose through which steam is conducted.

Radiator or condenser hose, through which a cooling agent at elevated temperature, e. g., glycol or glycerol, flows, is advantageously constructed of Buna rubber. Stability at elevated temperatures and resistance to oils are in many cases combined

with favorable results.   Special mixtures prepared from Buna N have been used successfully for hot oils, even at temperatures above 100° C.

Material for manhole gaskets, and packing for hot water pipes, for sublimation equipment and for steam vessels and pressure vessels of all kinds which have been made of heat-resistant synthetic rubber have given longer service than the corresponding products made of natural rubber.   Conveyor belts of artificial rubber have been manufactured for several years, and have demonstrated their utility where hot coke, ashes, and other hot material is conveyed.

Resistance to Abrasion

In so far as abrasion resistance is concerned, more is demanded of a tire tread than of any other rubber product.   The technical development of a tire, to the point to which it has been carried today, can be traced back for about thirty years. The short period which has elapsed while Buna rubber was being developed has already led to very satisfactory results.   Today it is possible to manufacture from Buna rubber a passenger car tire which has much better resistance to abrasion than does a similar tire made with natural rubber.   Giant tires are in process of development, and it is to be hoped that here too tangible results will soon be forthcoming. Although the problem of manufacturing tires economically has not yet been solved, the fact should not be overlooked that special types of tires made of Buna rubber can be used advantageously, even at a higher price.

Besides tires, there are many other possible cases where the greater resistance to abrasion of the synthetic product can be utilized to advantage.   Conveyor belts which carry material having sharp edges, *e. g.*, rubble or ore, wear away at a very rapid rate.   Here the better durability of conveyor belts made of Buna rubber can be utilized economically.   Furthermore it is possible to manufacture heels and soles from Buna rubber which wear almost twice as long as those made of natural rubber. Likewise Buna rubber should be a suitable material for buffers, which must withstand particularly high abrasion.

Permeability to Gases

As already mentioned, artificial rubber, especially Buna N, is considerably less permeable to gases than is natural rubber.   In this respect, Buna N is a remarkably good material for balloon fabrics, for high vacuum packings and for stoppers where impermeability to air and other gases is required.

Aging

Good aging is one of the most important properties which every rubber article is expected to exhibit.   It is obvious that the superior aging properties of Buna rubber give the latter a preëminent position over natural rubber from this point of view.   There are cases where it is difficult for instance to replace an installation of rubber, and therefore particularly severe requirements with respect to aging are made.   In this connection the relatively slight tendency of Buna rubber to exhibit fatigue-cracking is of importance.   Buna rubber excels natural rubber in this respect, and therefore is an important factor in obtaining stability of rubber goods, where mechanical requirements are changing rapidly.

Rubberized clothing, various protective coverings, waterproof cloaks and boat fabrics are generally destroyed by the action of light.   The superior resistance of artificial rubber in this respect is easily evident, and its use makes possible the fabrication of articles of these kinds with much greater useful service.

Because of its better resistance to ozone, Neon wiring and ignition cables made from Buna N rubber will be a valuable addition to available materials.

Hard Rubber

The unusual properties of Buna hard rubber render it extremely valuable in many applications, and its slight tendency to swell compared with natural hard rubber makes it of considerable value for linings in the chemical industry. Pipes and other equipment protected with Buna rubber can with perfect safety be used for powerful solvents like benzene and nitrobenzene. Experiments already carried out on this subject have shown that Buna hard rubber is unquestionably more suitable than natural hard rubber for such purposes.

The superior resistance of Buna hard rubber at elevated temperatures makes possible more extensive applications of hard rubber as a lining material for vessels, pipes, etc.

Buna hard rubber is also well adapted for distillation tubes, steam pipes, and pressure vessels which are exposed to temperatures of 150° C. or higher. It must of course be borne in mind in the use of such types of equipment lined in this way with Buna hard rubber that the latter is more brittle than natural hard rubber. As a result, Buna hard rubber lining has a greater tendency to crack when the iron expands with heating.

Hard rubber made from natural rubber is attacked only very slightly by most acids, alkalies, and salt solutions. On the other hand, it is rapidly destroyed by concentrated sulfuric acid, hydrofluoric acid and powerful oxidizing agents like chloric acid and nitric acid. Buna hard rubber is more resistant to these reagents, and this has rendered it almost indispensable as a lining material for various purposes. The extra work necessary in the processing of Buna rubber is more than compensated by the valuable properties of the final product.

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Fatigue in Rubber

Part I

A. B. D. Cassie, Maldwyn Jones, and W. J. S. Naunton

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Introduction.—The work described in this paper was undertaken to gain a closer knowledge of the cause of fatigue, and effects which result largely from fatigue, such as flex-cracking, and to put the laboratory testing of flex-cracking on a more reliable basis. Concordant results are difficult to obtain with present technic. This undesirable state of affairs must not be confused with the question of the value of laboratory testing in its relation to service. A certain laboratory test such as, for example, resistance to abrasion may bear no relation to the road abrasion result, but yet may be easily reproducible in the laboratory. On the other hand carefully selected laboratory results obtained in resistance to flex-cracking appear to bear a close (but possibly less exaggerated) relation to road tests; yet repetition in the laboratory may result in abnormally good or bad results without any apparent explanation.

Flex-cracking is a question which, with the decrease in the size of rims and increase in the use of giant pneumatics for fast passenger busses is becoming rapidly more important. Not so very long ago the quantity of gas black and accelerator were selected for maximum resistance to abrasion, but there has been a tendency during the last year or two to go back from the fifty towards the forty per cent mark for gas black content and to consider the accelerator as much from the point of view of resiliency as of resistance to abrasion. This is not surprising when one keeps in view that the tread of a modern giant pneumatic with its comparatively rigid sidewalls and its high inflation pressure is approaching to some extent the old solid tire, which conversely can be regarded as a pneumatic with an infinite inflation pressure. It is true that flex-cracking can be reduced by proper attention to tread and carcass design (cf. Grote, *Rubber Age* (N. Y.), **38,** 327 (1936)); nevertheless, by the use of certain chemical anti-flex-cracking antioxidants, it is possible to return to the old concentrations of gas black with improvement in mileage combined with as good or even better resistance to flex-cracking inherent in the rubber itself.

In spite of the work of Neal and Northam (*Ind. Eng. Chem.*, **23,** 1449 (1931)) a brief consideration of the position indicated that oxidation was only one factor in flex-cracking. The very fact that the order of effectiveness (Fig. 1) of antioxidants as such is entirely different from their order as anti-flex-cracking reagents pointed to this conclusion. Many other considerations, such as the bad flexing characteristics of super-aging low-sulfur vulcanizates, effect of cure upon flexing life, effect of repeated resting during flexing, and so on, confirm this conclusion. Furthermore, it has not been possible to confirm in this laboratory that the use of oxygen-absorbing substances (in presence of bases and normal antioxidants) produces any greater improvement in flex-cracking resistance than the normal antioxidant itself.

The authors were therefore forced to the conclusion that an important factor is fatigue resulting from internal friction. It is true that the relative importance of these factors depends upon such variations as the thickness of the sample, but there is little doubt that fatigue, if not the most important, is always an important factor

in this effect. Furthermore, internal friction in rubber is almost entirely due to the nature and dispersion of the filler. It therefore follows that for this investigation there must be available a technic for the evaluation of: (1) the dynamic Young's modulus and rigidity, together with associated frictional losses of samples of cured rubber; (2) the aging characteristics of samples of cured rubber, and (3) some method of measuring change in internal structure due to either change in the rubber structure itself or dispersion of the gas black or both.
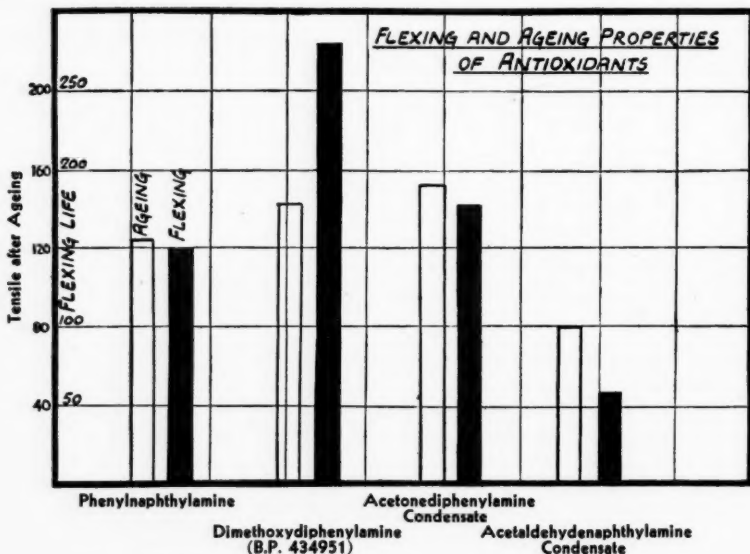

Figure 1

After careful consideration of all factors, the Geer oven method was selected for evaluating aging characteristics, and new methods were evolved for determining frictional losses and examining internal structure. The latter technic gives a sorting test which eliminates almost entirely wide divergence of results, and it has been found possible in some cases to calculate flexing life of a vulcanizate from its Geer oven-aging characteristics and internal frictional losses. This relation is put forward with all reservation, and the realization that much more work must be done before generalizations of universal application can be established.

Frictional Loss.—Deformation of an elastic body under any given stress can be determined when Young's modulus and the rigidity modulus, or that associated with twisting of the test-piece, are known: in fact, elongation and rotation deformations from the basis of all others, and the elastic properties of a material, are specified only when these moduli are given. Associated with the two moduli are two corresponding frictional losses; measurement of these will complete the specification of the mechanical properties of an elastic and plastic material such as rubber. Rubber, in practice, is regarded as incompressible: this means that Young's modulus and the rigidity modulus are not independent, and that determination of one should be sufficient. There is no reason, however, for assuming that the two fundamental internal frictional force coefficients are independent, and an investigation of frictional forces requires investigation of both.

Frictional losses can only be measured by dynamic methods; these also give convenient and accurate methods of measuring the elastic coefficients, particularly for small deformations. The rigidity modulus and its associated frictional loss are determined from torsion oscillations of a rubber test-piece, and Young's modulus and frictional loss from elongation oscillations.

Several authors (Mallock, *Proc. Roy. Soc.*, **46**, 233 (1889); Bouasse, *Ann. de la Faculté des Sciences de Toulouse*, **6**, 177 (1904); Thompson and Ellis, *Proc. Roy. Soc.*, **A148,** 171 (1935)) have determined the dynamic moduli and frictional losses of rubber from oscillation experiments, but unfortunately they do not give any details of the mixes used. Their results show that moduli and frictional losses can be more conveniently determined from these experiments than from measurements on hysteresis loops, but they are of little value in relating these quantities to fatigue or flex-cracking. The present paper includes experiments on various mixes using both torsion and elongation oscillations.
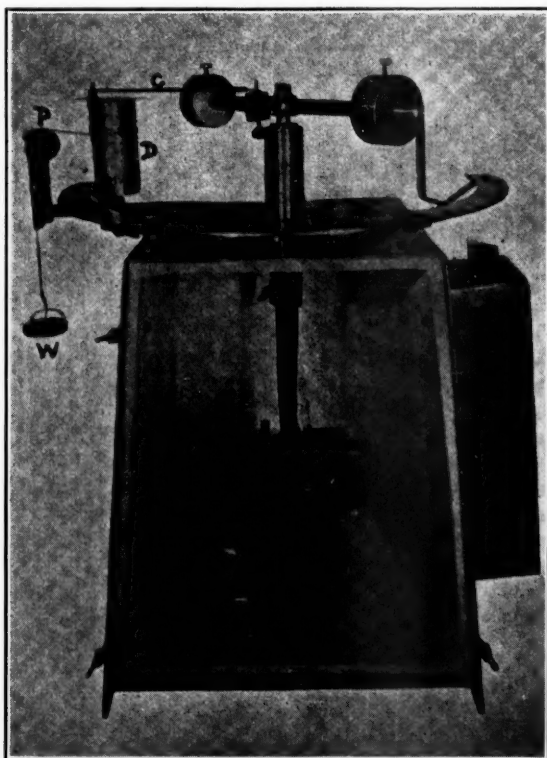

Figure 2

The torsion apparatus is shown in Fig. 2. It consists of a torsion head rigidly attached to the rubber test-piece, the lower end of the rubber being rigidly clamped to the base of the instrument. The torsion head consists of a rod $^5/_8$ in. in diameter; this carries two weights whose position on the bar can be varied to give the torsion

head any desired moment of inertia. The torsion head swings in a horizontal plane, the vertical axis being carried by ball bearings. The position of the lower clamp may be varied to take test-pieces of different lengths; the usual test-piece is of rectangular cross-section 1 in. by $1/2$ in., and 7 in. long. The rubber test-piece is enclosed in a housing for experiments at higher temperatures.

Theory.—If the rubber be free from friction and permanent set, the equation of motion of the system consisting of the twisted rubber and the torsion head, is to a first approximation

$$I \frac{d^2\theta}{dt^2} + \alpha\theta = 0$$

where θ is the angle through which the sample is twisted. This equation assumes Hooke's law to be valid, an assumption that restricts the oscillations to small amplitudes. The accurate equation would contain terms in θ^2 and higher powers of θ. The constant α is given for a circular cross section by

$$\alpha = \frac{\pi n a^4}{2l}$$

where α is the radius of the section, l is the length of the test-piece, and n is the rigidity modulus. The sample actually used is of rectangular section, and α will depend to a small extent on Young's modulus, but the rigidity modulus will primarily determine the motion.

The equation of motion so far discussed takes note of the elastic properties of rubber, and it must be extended to include the second feature of rubber, namely, its capacity of absorbing energy. Energy is continually lost within the system, and this can only occur if there are, acting within the system, forces dependent on speed, in the present case dependent on $(d\theta/dt)$. A first approximation to the mechanism of energy absorption must therefore be a force $b\,(d\theta/dt)$, where b depends on the energy absorption or frictional properties of the rubber and on the dimensions of the test-piece. The equation of motion of the system is now

$$I \frac{d^2\theta}{dt^2} + b \frac{d\theta}{dt} + \alpha\theta = 0$$

The accurate equation would include terms in $(d\theta/dt)^2$ and higher powers of this quantity; but just as Hooke's law has been assumed to determine the elastic properties, the linear term $(d\theta/dt)$ alone is supposed to determine the frictional properties. If, then, α and b can be determined, first approximations to the elastic and frictional properties will be known.

The solution of this equation is

$$\theta = \theta_0 \, e^{-\frac{bt}{2I}} \sin \frac{2\pi}{T}$$

where T is approximately $2\pi/\sqrt{\alpha/I}$ or $n = \frac{8\pi I l}{T^2 a^4}$.

T is the time required for one complete oscillation, and is obtained by direct measurement. Clearly, if the dimensions of the sample and I be kept constant, I/T^2 will measure the rigidity modulus.

Again, the ratio of the amplitudes of two successive swings is

$$\frac{\theta_0 e^{-b(t+T)/2I}}{\theta_0 e^{-bt/2I}} = e^{\frac{bT}{2I}} = e^{-\lambda T}$$

Each amplitude can be measured and their ratio will give λ or $b/2I$, since T is known. This factor depends only on the internal friction of the test-piece, the dimensions of the test-piece, and on I. The last two factors can be maintained constant, so that λ measures the frictional loss of the sample in question.

Hence, to compare the rigidity modulus and associated frictional loss of different samples, one requires to observe T, and the amplitudes of successive vibrations. In practice, decrease in amplitude is so rapid that the amplitudes of successive half-vibrations are used. The ratio of these is given by

$$\frac{\theta_2}{\theta_1} = e^{-\lambda T/2}$$

$$\text{or} - \lambda = \frac{2}{T} + 2.3 \log_{10} \frac{\theta_2}{\theta_1}$$

This analysis of elastic and frictional losses ignores the constant finite force required to shear a plastic body; the force responsible for permanent set. This constant force is independent of the elastic restoring forces; it does not affect the period, T, of the oscillation which still measures only the elastic rigidity coefficient, n, as if the rubber were perfectly elastic without frictional or plastic properties. The effect of this constant plastic force is to shift the origin by a constant amount at the beginning of each half-swing: this is reflected in a decrease in amplitude, so that λ includes not only the viscous frictional loss, but effects due to permanent set. At large amplitudes the permanent set contribution to λ is small compared with the viscous or true frictional contribution; this is verified by noting the drift of ratios of half-amplitudes of vibration.

Table I indicates the method of determining λ. It also gives the variation of T and λ with temperature.

The above method of determining frictional losses is known as the logarithmic decrement method: it is rather laborious when many samples have to be tested. Accordingly the apparatus (Fig. 2) was modified to measure frictional loss in terms of the energy given to the system by a falling weight. The weight (W) is attached to a string passing over a pulley (P) to a drum (D) rotating on a vertical axis. A pin attached to the disc top of this drum drives a crank (C) which in turn moves the torsion head. The motion of the torsion head end of the crank is simple harmonic, and this is roughly the motion of any point on the torsion head; hence this arrangement of the falling weight will maintain oscillation of the system provided the weight is great enough to overcome the frictional loss of the rubber test-piece. The minimum weight required to maintain oscillation will measure the frictional loss of the test-piece. This method has proved both convenient and accurate for measurement of friction losses associated with torsion.

Figures 3 and 4 show the variation of frictional loss and modulus with temperature: they also give a rough idea of the variation on changing from 40 parts of gas black to acetylene and lamp blacks. One notes that the modulus of the gas and acetylene black samples decreases with increasing temperature, whereas that containing lamp black increases much as the almost pure rubber mix (Crepe rubber, 100, zinc oxide, 5, zinc stearate, 1.5, sulfur, 2.0, diphenylguanidine, 1). This means that the presence of lamp black contributes little to the modulus, or does not reinforce the rubber toward small deformations.

Before determining the effect of different chemical components on tire tread mixes, one must determine the effect of change in cure. Frictional loss associated with torsion oscillations increases slowly with cure, particularly near the optimum cure.

TABLE I

BASE MIX: Smoked sheet rubber, 100; gas black, 40; zinc oxide, 5; sulfur, 3.25; stearic acid, 4; diphenylguanidine, 1.25

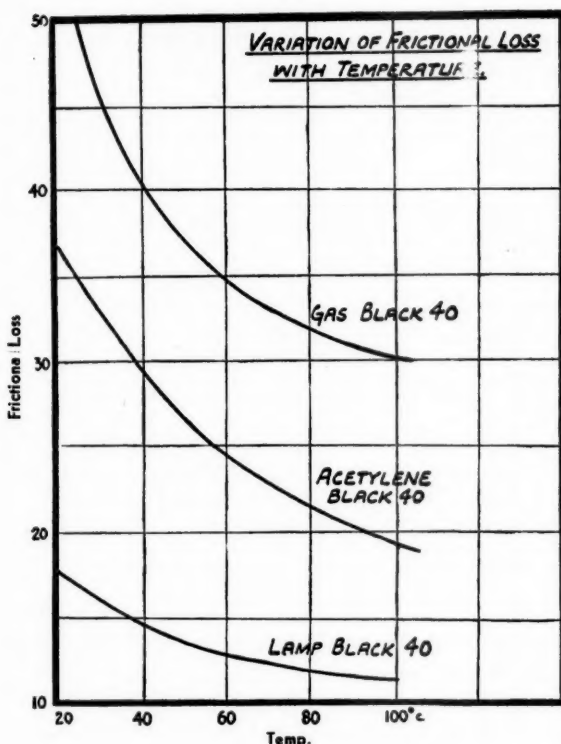| Osn.	Room Temp. Amp.	Ratio	50° C. Amp.	Ratio	90° C. Amp.	Ratio	100° C. Amp.	Ratio	110° C. Amp.	Ratio	Cooled 2 Hrs. Amp.	Ratio
0/2	16	$I.e.$, 11/16 = 0.69	16	0.71	16	0.75	16	0.75	16	0.78	16	0.66
1/2	11	$I.e.$, 8/11 = 0.72	11½	0.70	12	0.75	12	0.75	12½	0.76	10½	0.69
2/2	8	$I.e.$, 5/8 = 0.63	8	0.69	9	0.77	9	0.77	9½	0.74	7¼	0.62
3/2	5	$I.e.$, 3¾/5 = 0.73	5½	0.73	7	0.75	7	0.75	7	0.79	4½	0.72
4/2	3¾	Mean 0.69	4	Mean 0.70	5¼	Mean 0.75	5¼	Mean 0.75	5½	Mean 0.77	3¼	Mean 0.67
5/2	T = 3.2 sec. = 0.23		T = 4.2 sec. = 0.17		3½ T = 4.5 sec. = 0.13		3¾ T = 4.4 sec. = 0.13		3¾ T = 4.5 sec. = 0.12		T = 3.3 sec. = 0.24	

Figure 3

TABLE II

Mix: Smoked sheet rubber, 100; gas black, 40; zinc oxide, 5; stearic acid, 4; sulfur, 3.25; diphenylguanidine, 1.25

	Room Temperature			100° C.		
Cure	Wt. (G.)	T	$1/T^2$ or Modulus	Wt. (G.)	T	$1/T^2$ or Modulus
60'	47	3.1	104	22	4.0	62
90'	50	3.0	110	25	3.6	80
120'	53	2.9	120	28	3.5	82

Cure is at 40 lb. steam pressure

Table II reproduces a characteristic set of results. The moment of inertia and dimensions of the test-piece are kept constant, so that $1/T^2$ measures the modulus of the sample; this is multiplied by 1000 in Table II to give results in convenient units. One notes that the modulus also increases with cure.

The variation of torsion frictional losses with cure is small near the optimum cure, and any great change in frictional loss with change in a component of the mix may be safely ascribed to this change. Antioxidants in the concentration of 1 per cent on the rubber showed distinct though small effects on frictional loss. Increase of the antioxidant to 5 per cent will magnify these effects; provided this large antioxidant content has little effect on cure, the magnified effects will truly represent the good or bad effects of the antioxidant on frictional loss. Table III contains
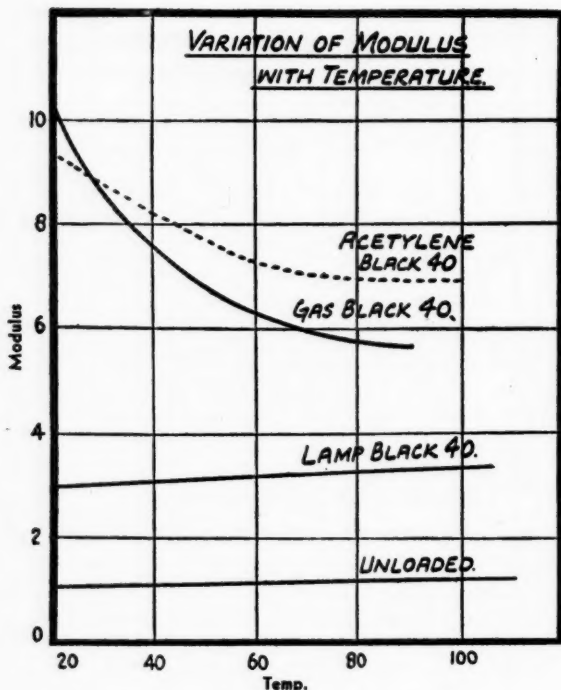
Figure 4

results for antioxidants that had little effect on cure when added to the extent of 5 per cent.

Several hundred potential antioxidants have been examined in the course of this work but the published results have been restricted to those obtained with four or five typical products.

The values obtained at 100° C. reveal most clearly the effect of different antioxidants; they are also found to be less subject to previous history of the test-piece. Table III, therefore, indicates that phenylnaphthylamine and dimethoxydiphenyl-

TABLE III

FRICTIONAL LOSS OF SAMPLES CONTAINING 5 PER CENT ANTIOXIDANT

A.—BASE MIX: Smoked sheet rubber, 100; gas black, 40; zinc oxide, 5; stearic acid, 4; sulfur, 3.25; diphenylguanidine, 1.25

Antioxidant	Cure	Room Temp.			100° C.		
		Wt.	T	$1/T^2$	Wt.	T	$1/T^2$
Nil	80′	60	2.6	148	28	3.3	90
	100′	60	2.7	137	27	3.4	86
Phenylnaphthylamine	80′	75	2.7	137	28	3.5	82
	100′	72	2.6	148	30	3.4	86
Dimethoxydiphenylamine (E. P. 434951)	80′	120	2.3	189	28	3.3	90
	100′	115	2.3	189	35	3.2	98
Acetaldehydenaphthylamine condensate	80′	105	2.4	174	62	3.3	90
	100′	108	2.4	174	70	3.2	98
Acetonediphenylamine condensate	80′	105	2.5	160	40	3.4	86
	100′	105	2.4	174	40	3.1	104

B.—BASE MIX: Smoked sheet rubber, 100; gas black, 40; zinc oxide, 5; stearic acid, 4; sulfur, 3.0; mercaptobenzthiazole, 0.75

Antioxidant	Cure	Room Temp. Wt.	T	$1/T^2$	Wt.	100° C. T	$1/T^3$
Nil	80'	55	2.7	137	28	3.2	98
	100'	60	2.6	148	28	3.3	90
Phenylnaphthylamine	60'	60	2.7	137	25	3.5	82
	80'	62	2.7	137	27	3.3	90
Dimethoxydiphenylamine (E. P. 434951)	60'	75	2.5	160	28	3.2	98
	80'	80	2.5	160	27	3.4	86
Acetaldehydenaphthylamine condensate	60'	77	2.3	114	50	3.1	104
	80'	80	2.3	114	55	3.1	104
Acetonediphenylamine condensate	60'	80	2.6	148	40	3.1	104
	80'	80	2.5	160	37	3.2	98

amine have little effect on frictional loss, whereas the acetonediphenylamine condensate has a considerable effect, and the acetaldehydenaphthylamine condensate a large effect.   None of the antioxidants commonly used in the trade appears to decrease the frictional loss.

An attempt has been made to correlate these frictional losses with flexing properties.   The antioxidants of Table III all have well-known flex-cracking times on the du Pont belt machine, and also well-known aging properties as measured by drop in tensile strength on bomb and oven aging.   One would expect that the greater the drop in tensile strength, the less would be the flexing life; a simple mathematical expression of this hypothesis is given by

$$F = \frac{K}{T_0 - T}$$

where F is the flexing life $(T_0 - T)$ is the drop in tensile, and K is a constant. Again, the greater the frictional loss, the less should be the flexing life; simple mathematical expression of this gives

$$F = \frac{K}{T_0 - T} - \alpha f$$

where f is a measure of the frictional loss, and α is a constant, f can be taken as the frictional loss of the test-piece containing 5 per cent of antioxidant.   The constant K and α can be determined if F $(T_0 - T)$, and f are assumed for any two test-pieces; the sample without antioxidant can be used in the correlation as F $(T_0 - T)$, and f are quite as definite for it as for those with antioxidants.

Following this procedure, correlation is obtained when oven-aging results are used.   The sample without antioxidant and that containing phenylnaphthylamine have been used to determine K and α; they give

$$K = 30,000 \quad \alpha = 2.8$$

Table IV indicates the agreement obtained for the other antioxidants.

TABLE IV

CORRELATION OF TIME TO FLEX-CRACKING WITH 3 WEEKS' OVEN AGING, AND INTERNAL FRICTIONAL LOSS

Antioxidant	Tensile Drop $(T_0 - T)$	Frictional Loss, f	Belt Flexing Life, F'	Flexing Life (Calc.)
Nil	200	28	70	(70)
Phenylnaphthylamine	128	28	160	(160)
Dimethoxydiphenylamine (E. P. 434951)	87	30	250	260
Acetaldehydenaphthylamine condensate	100	75	75	90
Acetonediphenylamine condensate	105	40	100	170

The large value of K does not mean that frictional loss contributes little to the results of Table IV; it is large only because it is divided by the large tensile drop figure. Thus for the acetaldenaphthylamine condensate the term $\dfrac{K}{(T_0 - T)}$ gives 300, and the frictional loss term 210.

The correlation of Table IV seems very good, particularly when one recalls possible experimental errors in the various quantities involved, and the very simple expression which has been used. It does seem to show that frictional losses play a large part in determining the flexing life of gas black-loaded rubbers.

Further confirmation of the importance of frictional losses is obtained from a study of elongation oscillations, or those dependent on Young's modulus and associated frictional loss.

The apparatus is shown in Fig. 5. It consists of a torsion head, T carried by a bearing, B. The lower end of the axle carries an arm, A, to which is attached the
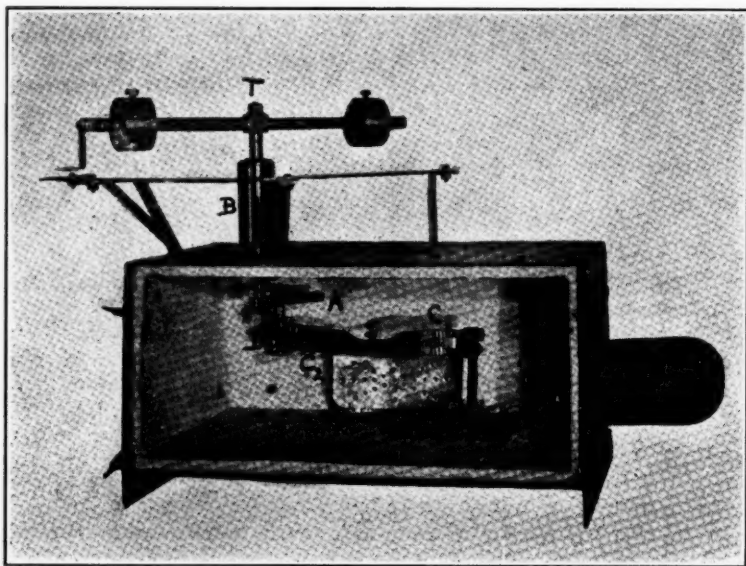

Figure 5

clamp C_2. This clamp pivots on the bearing D. The rubber test-piece S is held by C_2 at one end, and by a fixed clamp, C_1, at the other. Rotation of the torsion head elongates S, so that T and S form an oscillating system. $1/T^2$, where T is the time of swing, is proportional to the dynamic Young's modulus. The frictional loss can be determined by the logarithmic decrement method, or by the falling weight method. The latter is not always successful in the present case, as the oscillations are rather far from simple harmonic.

The moment of inertia of the torsion head can be varied by moving the weights along the rod T.

The amplitude of elongation during oscillation can be varied by moving C_2 and D along the arm A, and the initial elongation can be varied by moving the clamp C_1.

Test-pieces are cut from Schopper sheets 3 to 4 mm. thick. The dumb-bell type

was finally adopted.   Ordinary strips of the order of 1 cm. wide were tried, but proved unsatisfactory due to the clamps producing thin sections; there is no increase in width at the clamps to nullify the effect of this thinning of the test-piece, and much of the elongation will therefore occur near the clamp.   The dumb-bell type with its wide end pieces overcomes this difficulty.

The first point investigated with this apparatus was variation of frictional loss with elongation.   Tire tread mixes show a surprisingly large decrease in frictional loss with increase of initial elongation.   Figure 6 gives some idea of the decrease observed.   This large decrease was first suspected to be due to increase in speed of

Figure 6
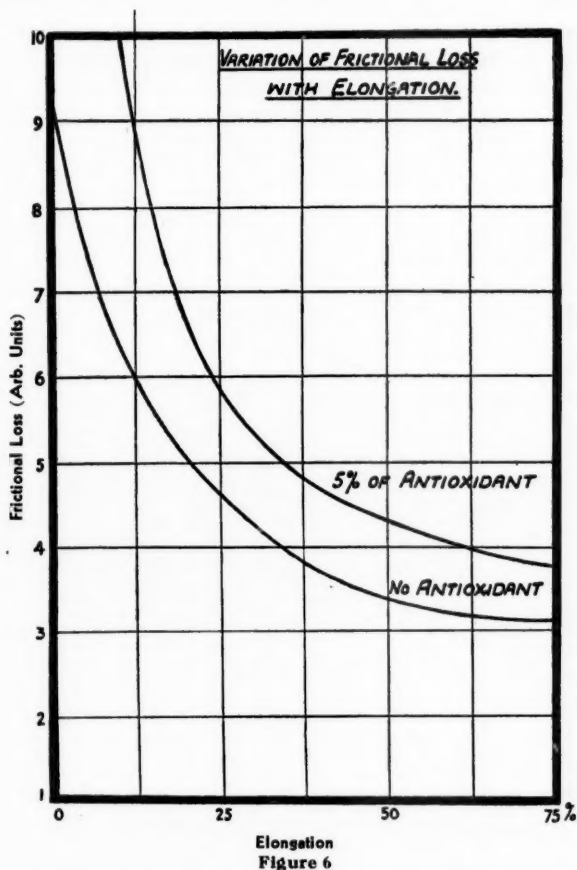
oscillation with increasing initial elongation; at the lower elongations the elastic modulus is low, giving a slow period of vibration, and the slower rubber is worked the more pronounced is its plastic properties.   This explanation was easily shown to be incorrect.   This period of oscillation can be decreased by decreasing the moment of inertia of the torsion head.   This was accordingly decreased until the period of oscillation at 25 per cent initial elongation was equal to that at 75 per cent; the decrease in time of oscillation produced no appreciable change in frictional loss

at 25 per cent elongation, so that the increasing frictional loss with decreasing elongation is not due to change in speed of oscillation.

If the hypotheses used to correlate fatigue or flexing life with aging and frictional loss be correct, the above result means that much of the deterioration associated with fatigue occurs near zero deformation of the test-piece. This has been directly verified. The rocker fatigue machine (Fig. 7) repeatedly stretches a strip of rubber,
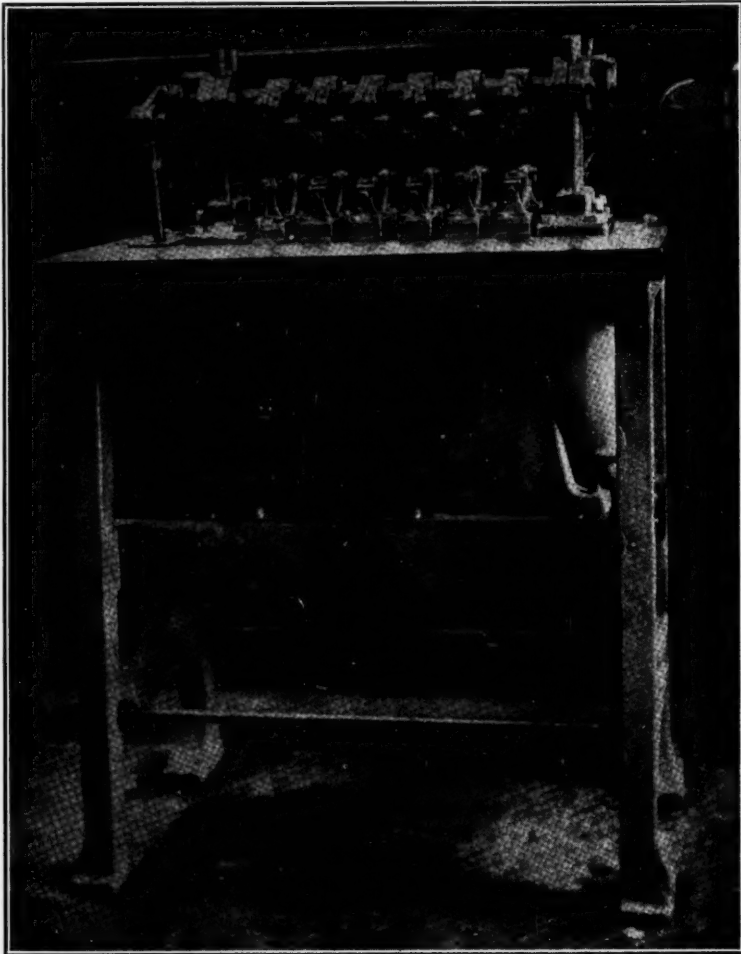

Figure 7

the strip returning to zero elongation at the end of each cycle. An automatic micrometer take-up was designed for this machine to prevent the strip returning to zero elongation. It is illustrated in Fig. 8. The clamp C normally fixed to the base of the apparatus is attached to a rod, R, of square, $1/2$ in. by $1/2$ in. cross-section; this passes through guides, and is threaded on its lower end. On this thread is the
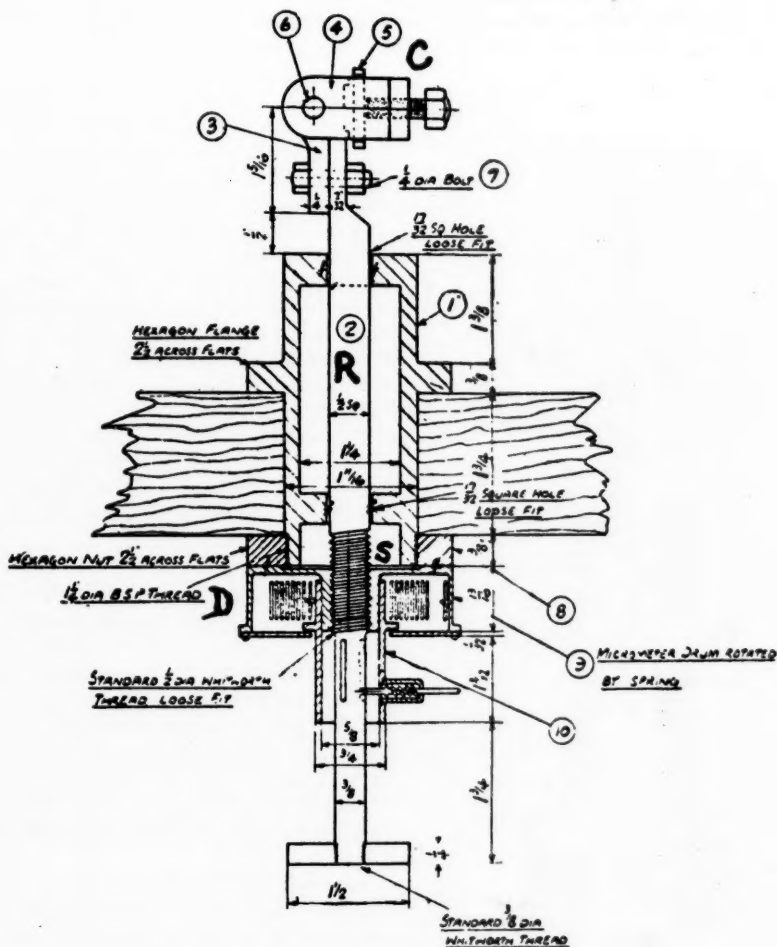
Figure 8(a)

drum D. This contains a clock spring that rotates the drum until it is in contact with the surface S. The weight of the clamp, rod, and drum, together with added weights if necessary, keep the test-strip under tension at the bottom of the stroke: as permanent set occurs so that the weight is sufficient to separate D and S, the spring rotates the drum up to the surface and maintains the original condition of stretching. Thus, the tension in the strip never drops below any chosen value.

Test-strips run in this manner, so that zero elongation was never attained during the test, lasted for exceptionally long periods; a tire tread with no antioxidant actually outlasts those with the best of anti-fatigue antioxidants when the latter return to zero elongation. In general, the time required to break a test-piece that does not return to zero elongation is anything from 4 to 10 times that required when it does return to zero elongation. Even test-pieces that have been ozone-cracked outlast the ordinary test-piece returning to zero stretch. These experiments show

that fatigue largely occurs near zero deformation, and this is precisely where frictional forces become very large, hence they must contribute largely to fatigue deterioration of the rubber.

It follows, too, that a tire which has been molded in such a way that when inflated is under stretch, will give a longer flex-cracking free life due to this effect.

Cooper (*Ind. Eng. Chem., Anal. Ed.*, **2**, 392 (1930)) and Busse (*Ind. Eng. Chem.*, **26**, 1194 (1934)) have already drawn attention to the importance of low elongations in flexing and tearing experiments. Busse concludes that gas black loaded rubber develops "mechanical fibers" on stretching, and that these are highly resistant to tear; in fact, once these have been developed, flex-cracking resistance is adequate. Thus a study of the mechanical fibers will give little information relating to fatigue or flex-cracking, and one must look for solution of this problem in the properties of rubber before the fiber structure is developed. Internal frictional forces are the most likely source of fatigue for, apart from the heating they produce, their presence implies a continual change of structure, and this change, unlike that associated with the stretching of elastic fibers, is irreversible or permanent: it is, in fact, fatigue as distinct from chemical deterioration. Thus the work of Cooper and Busse, together with results already quoted in the present paper, all point to fatigue originating in frictional losses near zero elongation.

The introduction has mentioned that elongation and rotation deformations form the basis of all others, and that the frictional losses associated with these basic deformations need not follow the same course. Belt flexing is an elongation deformation and the appropriate frictional losses will be determined from elongation oscillations. Frictional losses at very small elongations are difficult to determine because of the difficulty of obtaining accurate setting of small initial elongations. Torsion oscillations automatically pass through zero deformation twice per cycle, and are therefore ideal for determining the important
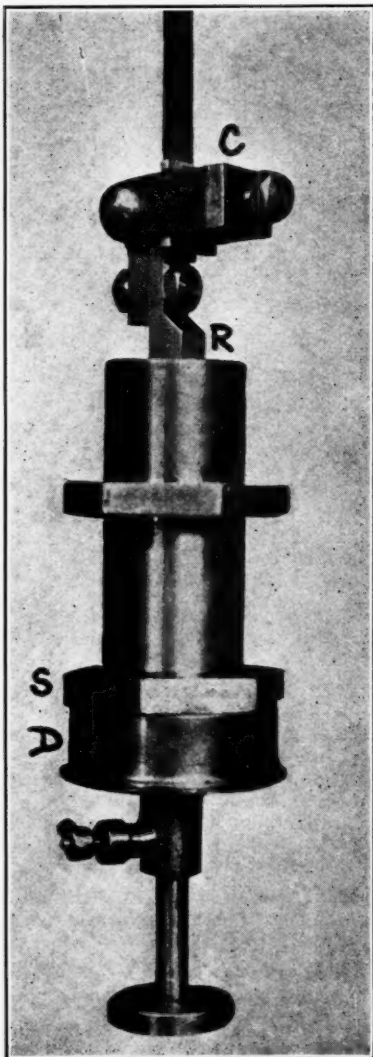

Figure 8(*b*)

frictional losses near zero deformation. These results will only be of value, however, if elongation and torsion deformation losses follow the same course. This

does not appear to be generally true; results quoted below show correlation only in some cases with the torsion results.

Table V gives a typical set of results on variation of elongation frictional loss with cure.

<center>TABLE V</center>

<center>VARIATION OF FRICTIONAL LOSS AND YOUNG'S MODULUS WITH CURE (FALLING WEIGHT METHOD)</center>

BASE MIX: Smoked sheet rubber, 100;   gas black, 40;   zinc oxide, 5;   stearic acid, 4;   sulfur, 3.25;   diphenylguanidine, 1.25

Initial Elongation, 40' Cure	Wt.	T (4 Osns.)	$1/T^2$	$(1/T^2)/$Wt.
14%	37	7.2	19	0.5
28	30	6.5	24	0.8
43	24	6.3	25	1.05
57	20	6.0	28	1.4
71	18	5.9	29	1.6
60' Cure				
14%	30	6.7	22	0.75
28	22	6.0	28	1.3
43	19	5.8	30	1.6
57	17	5.6	32	1.9
71	17	5.2	37	2.2
80' Cure				
14%	38	5.7	31	0.8
28	34	5.0	40	1.2
43	29	4.9	42	1.45
57	27	4.8	43	1.6
71	30	4.5	50	1.7

<center>Cured at 40 lb. steam pressure</center>

Table V shows that elongation frictional losses attain a minimum value near optimum cure; torsion losses increase slowly with cure. The last column gives figures for $(1/T^2)/$Wt. $1/T^2$ is proportional to Young's modulus for the test-piece, so that $(1/T^2)/$Wt. represents the elasticity developed per unit frictional loss: the ideal rubber, that without frictional loss, would have the value infinity for this factor, and the higher the value of this factor the more nearly ideal is the rubber. The values of this factor have been plotted against cure in Fig. 9 and show a maximum near optimum cure.

Antioxidants (Table III) that give high frictional losses for torsion oscillations seem in general to give high losses for elongation oscillations. Figure 6 shows the frictional loss—elongation curve for the mix of Table III containing no antioxidant, and 5 per cent of an acetaldehydenaphthylamine condensate. The difference between the curves is much as one might expect from the torsion oscillation results. One difference observed relates to dimethoxydiphenylamine; this gave a high torsion frictional loss at room temperature, but a low value at 100° C.; its elongation frictional loss is low even at room temperature. The last fact agrees with its being a good antiflex-cracking antioxidant. One concludes, then, that frictional losses associated with the two basic deformations, elongation and torsion, do not, in general, follow the same course, and a determination of frictional losses really requires measurement of both.

Elongation deformations are probably more frequently encountered than torsion deformations, and in view of the lack of correlation of the two, determination of
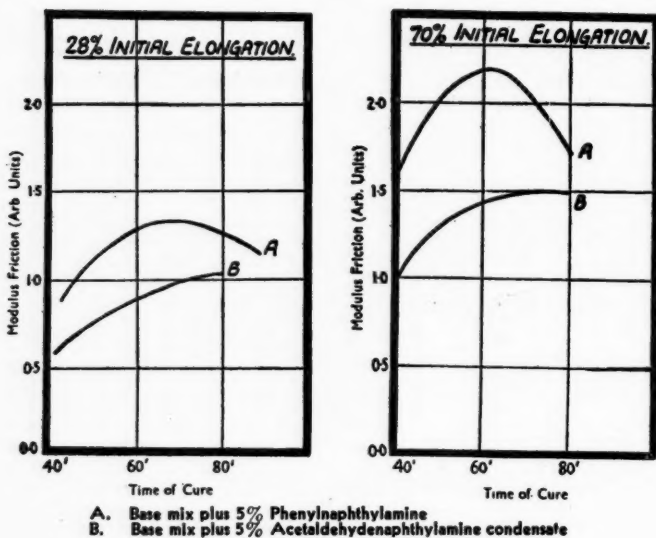
A. Base mix plus 5% Phenylnaphthylamine
B. Base mix plus 5% Acetaldehydenaphthylamine condensate

Figure 9

losses at low elongations becomes important. The logarithmic decrement method has been found more convenient than the falling weight method for these measurements. The theory of the logarithmic decrement method for this instrument is essentially the same as that for torsion oscillations, and need not be repeated. Measurements at low elongations require, however, a special use of the instrument in order to obtain the same initial elongation or stress for different samples. The torsion head is made unsymmetrical about its axis, and the apparatus is set slightly off the level position: this makes the torsion head swing away from the normal zero position. Accurate setting of the small initial stress is now obtained by sliding the stationary clamp towards increased elongation until the pointer of the torsion head reaches a predetermined mark on the scale.

At the low elongations thus obtained, damping is so great that oscillation persists for only one or two swings. The amplitude of each swing is determined, and the logarithmic decrement determined formula

$$A = A_o e^{-\lambda T}$$

$$\text{or } (\lambda T) = \log_e \frac{A_o}{A}$$

When so few oscillations are obtained, T cannot be measured with any accuracy; certainly within the limits of measurement, it is constant for different samples of the same gas black content. (λT) is therefore taken as a measure of frictional loss.

One point to note in this method is that the first swing will produce a high frictional loss: if now the elongation be reset, a lower value is obtained. This is the well-known phenomenon of the first hysteresis loop being considerably greater in area than subsequent loops. In practice the elongation is repeatedly reset until constant damping is obtained: the damping on the first swing can also be observed to measure the area of the first hysteresis loop.

Some results will be quoted:

The Mixes: Smoked sheet rubber, 100, gas black x, zinc oxide, 5, stearic acid, 4, sulfur, 3.25, diphenylguanidine, 1.25, where x is (1) 30, (2) 40, and (3) 50, gave for 60′ cure:

(1) $A_0 = 50°$, $A_1 = 43°$, $A_2 = 37°$. $(\lambda T)_1$ osn = 0.0645; $(\lambda T)_2$ osn = 0.135; *Mean* 0.066.

(2) $(\lambda T)_1$ osn = 0.086; $(\lambda T)_2$ osn = 0.167; *Mean* 0.085.

(3) $(\lambda T)_1$ osn = 0.107; $(\lambda T)_2$ osn = 0.223; *Mean* 0.110.

This means that the frictional losses are in the ratio of 1.69:1.29:1.00 for the black contents 50:40:30. Or, a 50-volume loading of gas black gives roughly 70 per cent greater frictional loss than the 30 loading, and the 40 gives roughly 30 per cent more than the 30. The effect due to neglecting any variation in time of swing is to minimize the difference in frictional losses; for T will be less the greater the gas black content, and the product (λT) will therefore increase less rapidly than λ with increasing gas black content.

TABLE VI

EFFECT OF 4 DAYS' BOMB AGING ON FRICTIONAL LOSS
λT

Antioxidant	Unaged		Aged		Increase		Tensile
	1st Osn.	Norm.	1st Osn.	Norm.	1st Osn.	Norm.	Drop
Phenylnaphthylamine	0.105	0.076	0.167	0.123	60%	62%	57%
Dimethoxydiphenylamine	0.101	0.076	0.135	0.097	34%	28%	48%
Acetaldehydenaphthylamine condensate	0.100	0.087	0.178	0.142	78%	64%	75%

The effect of bomb aging on frictional loss near zero elongation was investigated for the antioxidants: phenylnaphthylamine, dimethoxydiphenylamine, and acetaldehydenaphthylamine condensate; 1 per cent of the antioxidant was used in the base mix: Smoked sheet rubber, 100, gas black, 40, zinc oxide, 5, stearic acid, 4, sulfur, 3.25, diphenylguanidine, 1.25. The cure was 60 minutes.

The figures for the first oscillation cannot be accurate compared with those for the steady normal value. One notes that 1 per cent of the acetaldehydenaphthylamine condensate gives a frictional loss 14 per cent greater than phenylnaphthylamine or dimethoxydiphenylamine before aging. After aging, dimethoxydiphenylamine shows considerably less increase in frictional loss than the others: this agrees with its excellent flexing properties.

Table VII and Fig. 10 give a comparison of results obtained with the falling weight and decrement methods. The graphs show variation with initial elongation of the elasticity developed per unit frictional loss.

The adjusted values of $(1/T^2)/$Wt. given in the last column of Table VIIA, are those of the previous column multiplied by 4.65: this puts the elasticity developed per unit frictional loss on the same arbitrary scale for the two sets of observations. The conversion factor of 4.65 was actually obtained by dividing 2.6, the value for 8.5 per cent elongation with the decrement method, by 0.56, that obtained for the same elongation with the falling weight method. Thus, coincidence of the 8.5 per cent elongation values is not accidental: the closeness of values obtained for other elongations shows that the two methods agree surprisingly well in their estimates of frictional loss at the lower elongations.

Figure 10 also illustrates the remarkable decrease in elasticity developed per unit frictional loss as the initial elongation is decreased, and points once again to the importance of mechanical properties near zero elongation.
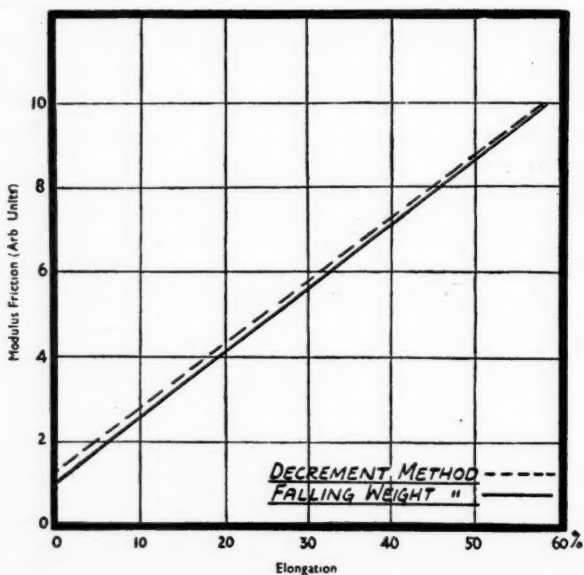
Figure 10

Extension and improvement of this work will depend on development of methods that determine mechanical properties near zero deformation. These methods are actually at hand in the form of sound-wave measurements, and a study of sound-wave propagation and absorption is likely to be well repaid; it would form a natural extension of the present work in the most promising direction.

The question now arises of the meaning of the change in frictional loss on addition of an antioxidant supposed to be chemically inert during vulcanization. If it is chemically inert, the change in frictional loss must be due to change in the physi-

TABLE VII

ELASTICITY DEVELOPED PER UNIT FRICTIONAL LOSS

Mix: Smoked sheet rubber, 100; gas black, 40; zinc oxide, 5; stearic acid, 4; sulfur, 3.25; diphenylguanidine, 1.25

A.—Falling Weight Method

Elongation	Time of 4 Osns.	Weight, Gm.	$(1/T^2)$/Wt.	$(1/T^2)$/Wt. Adjusted
$8^1/_2$	5.8	54	0.56	2.6
25	5.1	37	1.04	4.9
41	4.5	30	1.65	7.7
58	4.3	25	2.2	10.1

B.—Decrement Method

Elongation.	Osns. $50-30°$ (N)	Time of 10 Osns., Secs.	$\frac{N}{T}(=1/T^2/\lambda)$
$8^1/_2$	$3^3/_4$	$14^1/_2$	2.6
25	$6^1/_2$	13	5.0
41	9	12	7.5
58	11	11	10.0

cal structure of the rubber; the gas black dispersion or rubber matrix may have been changed. Is there, then, any method of measuring the internal structure of a sample of tire tread rubber? Mechanical or sound waves and long electromagnetic waves will both penetrate rubber and will measure its structure in different ways. The manner in which sound waves will measure this structure has already been indicated. The loss of intensity of longer electromagnetic waves will give a second measurement of structure; for gas black being a good electrical conductor compared with rubber proper, should show eddy current losses: the smaller the gas black particles the less these losses, and the less the loss of intensity of the wave. This is one source of loss of intensity, but Maxwell and Wagner have shown that the loss of intensity depends in a complicated manner on the general heterogeneity of the sheet traversed by the wave. The complicated nature of the loss of intensity is, however, irrelevant for the present purpose; the problem is whether or not the physical structure of tire tread rubber is changed by change of antioxidant, or even by change of any of the chemical components of the mix; such a change should be shown by change in the loss of intensity of an electromagnetic wave.
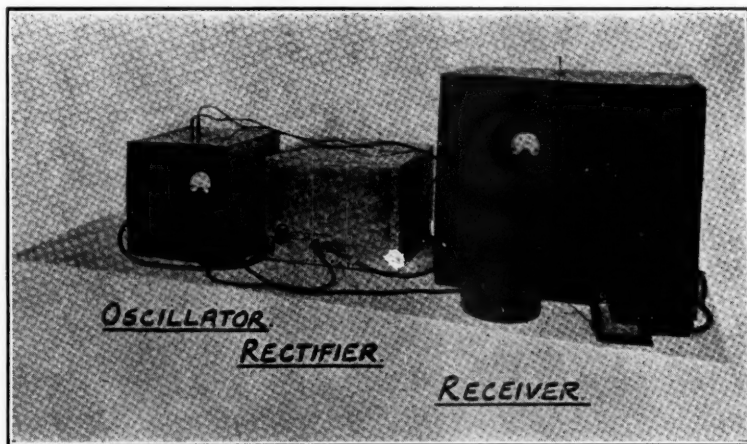

Figure 11

There are two possible methods of determing this loss of intensity. The rubber sample can be placed in an induction furnace, and its rate of rise of temperature determined. This heating will depend primarily on eddy current losses, and should therefore measure the gas black dispersion. The second method is to determine the electrical power factor of a sheet of the rubber. The energy lost by an electromagnetic wave in traversing a sheet of material is given very roughly by the electrical power loss or power factor of the sheet. This is easily measured for substances of high power factor such as tire tread mixes, and so provides just the measurement required to determine whether or not any given samples have one and the same physical structure. The early measurements reported in this paper have therefore been carried out by the power factor method, but a comparison of these with induction heating should enable one to distinguish changes in the rubber matrix from changes in gas black dispersion.

Apparatus for measurement of electrical power factor (Fig. 11) has often been de-

scribed (cf. Scott, McPherson, and Curtis, RUBBER CHEM. AND TECH., 7, 342 (1934)), and need not be dealt with in detail here. The arrangement of the test-piece is shown in Fig. 12. Waves of some 500 meters wave-length were used for the measurements. The power factor figures are quoted in arbitrary units. Absolute determination of
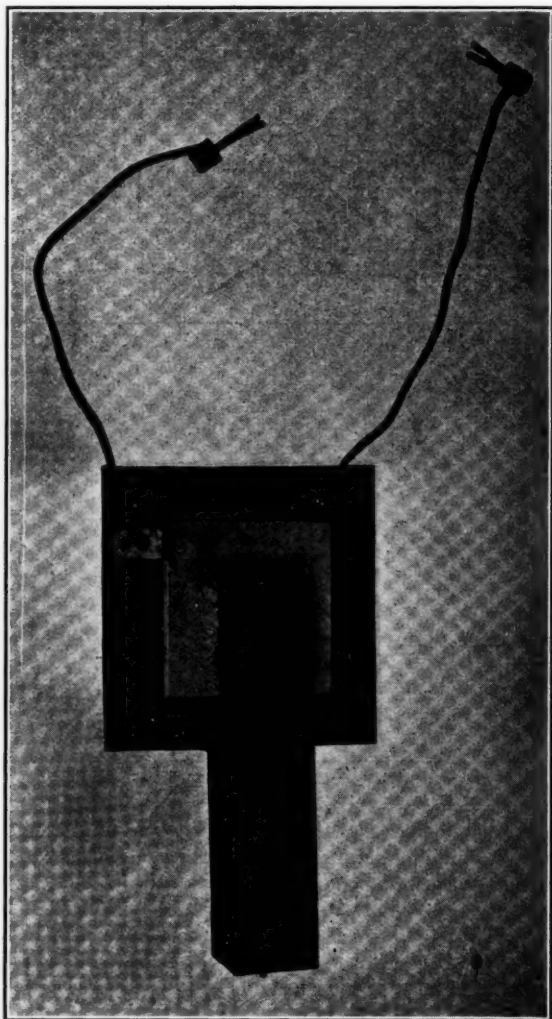

Figure 12

power factor values requires accurate determination of the wave-length used; this is superfluous for the present purpose, provided the wave-length is maintained constant, for only relative values are required. Experiments with gas black dispersed in vaseline show that even power factor measures to some extent the size of gas

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black agglomerates.   A sample of compressed black was passed through sieves of
decreasing size, so that the particles were arranged into the classes: (1) greater than
20 mesh; (2) 20–60 mesh; (3) less than 60 mesh.   Equal weights of these blacks
dispersed in a fixed amount of vaseline gave the results of Table VIII.

TABLE VIII

VARIATION OF POWER FACTOR WITH GAS BLACK PARTICLE SIZE

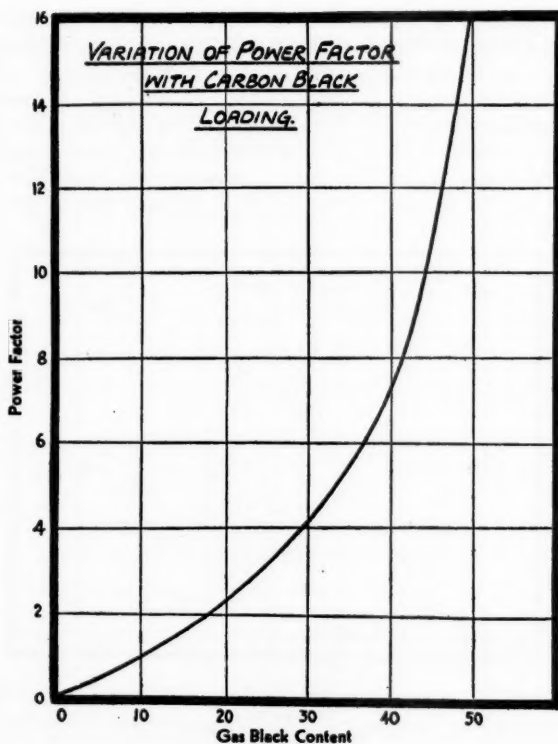| Size	> 20 mesh	20–60	< 60 mesh
Power factor	10	8.7	5.3

Figure 13

Thus, the hypothesis that power factor decreases with decreasing particle size,
appears to be corect.

Further confirmation of this hypothesis is given by measurements of the power
factor of rubber with different loadings of gas black.   Figure 13 shows the variation
of power factor with gas black content, and the individual results are given in
Table IX.

The curve of Fig. 13 has the shape one would expect from agglomeration with
increasing gas black content.   It again indicates that electrical power factor takes
note to some extent of gas black dispersion.

Figure 14 shows the remarkable increase in power factor with cure; it seems to
indicate in fact that agglomeration of the black takes place during cure.   The shape

VARIATION OF POWER FACTOR WITH GAS BLACK CONTENT

MIX: Smoked sheet rubber, 100; zinc oxide, 5; stearic acid, 4; sulfur, 3; mercapto-benzothiazole, 0.75. CURE: 45 minutes at 40-lb. steam pressure •

Gas black content	5	10	20	30	40	50
Power factor (arbitrary units)	0.4	0.9	2.2	4.0	8	16

of this curve shows that changes in structure due to change of antioxidant should be determined at optimum or greater cures, for beyond the optimum, power factor is not so sensitive to cure.

There was the possibility that rubber cured with an oxygen-free gas black might possess a different structure from rubber cured with the normal oxygen-containing gas black, because of the relative absence of oxygen cross-linkages. Gas black was therefore submitted to prolonged heating at 150° C. in a high vacuum, and further samples were heated to 500° C. in nitrogen (to destroy organic retarding agents of the type suggested by Schoenfeld, *Ind. Eng. Chem.*, **27**, 571 (1935)), and all products were cooled in nitrogen and milled into rubber in an atmosphere of nitrogen. There was only a slight increase (from 8–9 to 9–10) in power factor units, which
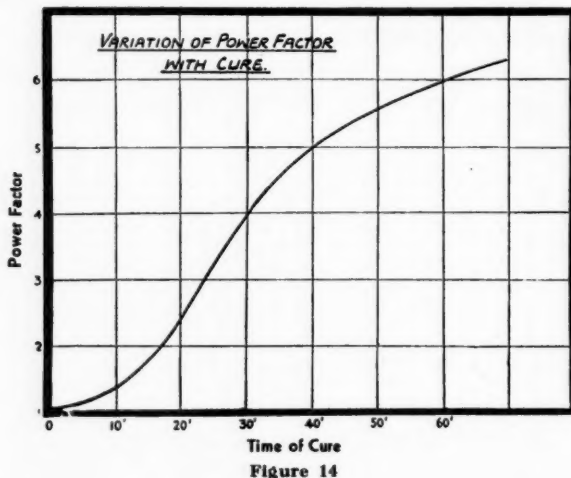

Figure 14

indicates there was no practical change in structure and furthermore there was no improvement in flex-cracking resistance.

On the other hand, similar mixes cured with oxygen (trinitrobenzene) instead of sulfur gave a value of 4–5 in electrical power factor units.

The power factor method applied to antioxidants does show that these can modify the rubber structure in such a way that the tensile strength remains unchanged. Acetaldehydenaphthylamine condensate was first investigated as this gives a large change in frictional loss; 1 per cent of this antioxidant gives a decrease in power factor, while 5 per cent decreases the power factor of the fully cured sample to roughly one-third of that without antioxidant.

Figure 15 gives the time-power factor curve for the base mix: Smoked sheet rubber, 100; gas black, 40; zinc oxide, 5; stearic acid, 4; sulfur, 3; mercaptobenzo-

thiazole, 0.75 with and without 5 per cent of acetaldehydenaphthylamine condensate. This change is not reflected in the time-tensile curves of the corresponding mixes. Phenylnaphthylamine and dimethoxydiphenylamine even at 5 per cent concentration show little or no effect on power factor, while acetonediphenylamine
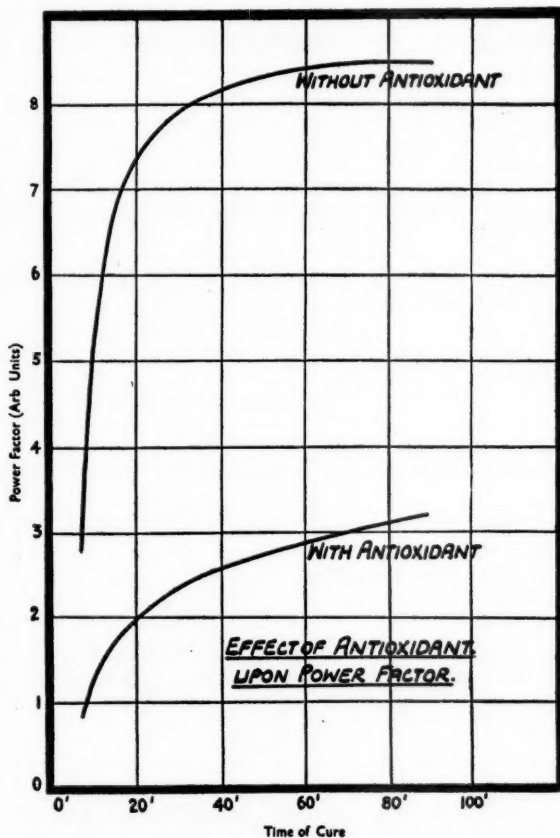

Figure 15

decreases it to an intermediate extent. Thus, there is no doubt that antioxidants apart from giving protection against oxidation, may modify the physical structure in a manner that is not reflected in routine physical measurement; only fatigue and flex-cracking measurements seem to bring out the hidden differences in structure.

In view of the claims made for oxygen-absorbing substances such as pyrogallol as flex-cracking resisters, the effect of such substances upon electrical power loss was studied. The use of 1 per cent of pyrogallol (in the presence of triethanolamine and a phenylnaphthylamine) brought the power loss figure down to 1–2 from the usual 8–9. The effect of pyrogallol (either with or without organic bases and even with increased accelerator and base) is so drastic that its effect is shown not only by the special methods developed in this investigation but also by routine physical measurements. It acts not as a true retarder of the speed of vulcanization but as an

BASE MIX: Rubber (smoked sheet), 100; zinc oxide, 5; gas black, 45; pine tar, 2; stearic acid, 4; sulfur, 3; phenylnaphthylamine, 1; mercaptobenzothiazole, 1

Mix		Amount	Cure, Mins. at 135° C.	Modulus (300%)	Tensile (Kg. per Sq. Cm.)	Belt Flexing (Hours)	Electrical Power Loss
Base			30	63	258	96	12.0
			45	89	286	120	11.4
			60	107	297	192	10.1
Base +	{ Pyrogallol	1.0	30	67	237	124	1.8
	Triethanolamine	1.0	45	80	243	192	2.0
			60	86	249	180	1.7
Base +	{ Pyrogallol	1.0	30	76	246	144	2.0
	Triethanolamine	1.5	45	84	245	. . .	2.4
			60	91	265	. . .	1.6
Base +	{ Pyrogallol	1.0	30	81	259	. . .	1.8
	Triethanolamine	1.0	45	94	270	. . .	2.0
	Mercaptobenzothiazole	0.5	60	98	259	180	2.0
			Mins. at 141° C.				
Base +	{ Catechol	1.0	45	90	274	216	12.0
	Triethanolamine	1.0	60	96	272	192	11.3
Base +	{ Hydroquinone	1.0	45	119	266	204	13.5
	Triethanolamine	1.0	60	115	267	192	11.8
Base +	{ Resorcinol	1.0	45	110	271	156	11.8
	Triethanolamine	1.0	60	112	273	168	10.3
Smoked sheet		100	30	84	261	. . .	. . .
Zinc oxide		5	45	104	283	208	14.2
Treated carbon black (1)		40	60	110	279	. . .	. . .
Stearic acid		4					
Sulfur		3					
Mercaptobenzothiazole		0.75					
Phenylnaphthylamine		1.0					
Ditto +	{ Pyrogallol	0.75	30	76	215	. . .	. . .
	Monoethanolamine	0.5	45	72	221	208	3.7
			60	75	191	. . .	. . .
Same, using treated Carbon Black No. 2			30	78	271	180	10.0
			45	76	250	. . .	. . .
			60	98	253	. . .	. . .

Note: Treated Carbon Black No. 1.—Heated at 500° C. (in nitrogen).
Treated Carbon Black No. 2.—Evacuated at 150° C.

apparent permanent inhibitor of the completion of vulcanization; for example, in a mix which normally gives at optimum cure a tensile strength (Schopper ring test) of 290 kg. per sq. cm., the presence of 1 per cent (on the rubber) of pyrogallol plus 1 per cent of triethanolamine drops the maximum tensile strength to about 240 kg. per sq. cm.

The great drop in electrical power loss cannot be due either to degree of cure or to alteration in dispersion of the gas black, and must therefore be due to a definite modification of the structure of the cured compound. Repeated trials (both with and without modification of the mixing procedure) have given an electrical power loss figure around 2, and when tested in the du Pont belt-flexing machine have shown no practical improvement in flex-cracking resistance.

The foregoing results are summarized in the following table.

Electrical power factor may be varied by many means other than change in anti-oxidant. The faster the rate of vulcanization the higher appears to be the power factor of the finished product. Long, low temperature cures can be used to give low power factors. A surprising fact regarding the many 40 per cent gas black mixes whose power factors have been determined is that all those mixes, which from the experience of road service have been adopted by the industry, seem to have power factors between 8 and 10 on the scale used in this paper. Rubber chemicals that give tire tread mixes (containing 40 per cent gas black) with power factors much outside this range are sooner or later discarded. This fact is purely empirical, and may be changed with time; but on the other hand, the structure represented by a power factor in this range is possibly just that best able to withstand service conditions.

The ease with which power factor measurements may be obtained, together with the manner in which they indicate the internal structure of tire tread mixes, suggest that they may be of use not only in research but also in factory control. Power factor is sensitive to milling procedure, and verifies the technologist's conclusion that repeated milling with resting periods improves dispersion. In short, power factor measurements seem to give rapid and sensitive determinations of the quality of tire tread rubbers, and could be readily applied to checking the uniformity of output.

Summary

1.   An apparatus is described for the measurement of the dynamic Young's modulus and associated frictional forces.

2.   A modified apparatus is described for the measurement of the rigidity modulus and associated frictional forces.

3.   The frictional loss of a rubber mixed with acetylene black is midway between the losses of rubbers mixed with gas and lamp black, respectively.

4.   The frictional loss of rubber mixed with any form of carbon black falls with increase in temperature.

5.   The moduli of rubbers containing gas and acetylene black decrease with increasing temperature, whereas those containing lamp black increase with increasing temperature similar to that of an unloaded rubber.

6.   Frictional losses increase with cure, but the change becomes small around the optimum cure.

7.   Antioxidants have a definite effect upon frictional loss quite apart from any effect due to alteration of degree of cure.

8.   The relation $F = \dfrac{K}{T_0 - T} - \alpha f$, where F is the flexing life in hours in the

du Pont belt machine, $(T_0 - T)$ is the drop in tensile strength on aging for three weeks in the Geer oven at 70° C., f is the frictional loss (torsional) at 100° C. of the test-piece containing 5 per cent antioxidant, and F and α are constants, appears to hold for several antioxidants. The relation cannot be established for all antioxidants as a concentration of 5 per cent of some commercial antioxidants renders satisfactory curing impossible.

9. It is shown that fatigue originates largely in frictional losses near zero elongation.

10. A modification of the Vogt machine, in which automatic correction is made for permanent set in addition to means of preventing the sample from returning to zero elongation, has been constructed to prove experimentally that rubber which is flexed while permanently under stress will last much longer than rubber which is allowed to return to zero elongation.

11. Frictional losses associated with the two basic deformations do not in general follow the same course.

12. The falling weight and decrement methods of determining Young's modulus were found to give consistent results.

13. Electrical power loss with waves of a fixed wave-length varies with the nature and the dispersion of conducting compounding ingredients, and the fundamental structure of the vulcanizate and can therefore be applied to detect changes in such factors.

14. The electrical power factor decreases with decreasing particle size of conducting fillers (such as gas black).

15. The electrical power factor of the vulcanizate increases with gas black content, and the increase becomes very rapid after a concentration of about 40 parts by weight of gas black per 100 parts of rubber.

16. The electrical power factor increases with cure, but the increase becomes small at the optimum cure.

17. The presence of pyrogallol (with or without the presence of an organic base) gives a vulcanizate with an abnormally low electrical power factor, which points to an abnormal structure in such vulcanizates.

18. Tire-tread type vulcanizates cured with trinitrobenzene in place of sulfur give low electrical power factors.

19. Catechol, hydroquinone, resorcinol, and indigo white do not give this abnormally low electrical power factor.

20. Electrical power factor measurements show that ordinary antioxidants can modify the physical structure of vulcanizates in a manner not necessarily reflected in routine physical measurements.

21. Electrical power factor measurements can be used for detecting abnormal vulcanizates (due to any cause such as processing, past history, abnormal curing, etc.) which are unsuitable for routine flex-cracking determinations.

22. Electrical power factor determinations which can be made in a few minutes are put forward as routine factory process control tests.

23. Gas black freed from oxygen either by heating *in vacuo* or in a steam of nitrogen does not give any practical improvement in flex-cracking.

24. No practical improvement can be found in the flex-cracking of vulcanizates cured with the addition of pyrogallol or similar oxygen-absorbing substances and bases.

Hardness of Vulcanized Rubber at Low Temperatures

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Introduction

It is a well-known fact that vulcanized rubbers "freeze," *i. e.*, become very stiff, at low temperatures. The author has measured quantitatively the increase in hardness with decrease in temperature, including the rate of this change, and has also attempted to prepare rubber which does not harden at low temperatures.

Though there are many types of apparatus for estimating hardness, all are based on the penetration of a needle with dull point into the rubber, the depth depending on the load applied on the needle. The author has constructed a simple apparatus based on this principle.

The hardness of raw rubber and rubber-sulfur vulcanizates was tested from room temperature down to −50° C. The effects of softening agents, reclaimed rubber and accelerators in the rubber-S base mixts. were also studied.

Apparatus for Estimating Hardness

Figure 1 shows the construction of the apparatus. A definite load is applied on a needle and the hardness is expressed by the depth or penetration of the needle without breaking the rubber.

A is a round brass disc 35 mm. in diameter and 1 mm. thick, mounted on a cylindrical support, B, carrying a steel needle, C, with a dull point. B is held by a vertical pipe, E. The test-piece is placed under C, the line D is adjusted to the cathetometer (reading to 0.01 mm.), a definite load is applied on A. The reading of the cathetometer with the D line gives the depth of penetration. The whole apparatus, except that of cathetometer, is placed in a thermostat (sensitivity ±0.1° C.) kept at a low temperature by "dry-ice" (Fig. 2), and is so constructed that the load can be applied without opening the apparatus. Friction between B and E is very small.

The total weight of the movable portions, A, B, C, and D is 40 grams. With a load of 500 grams, the total load is 540 grams; therefore, the construction of the movable portion should be as light as possible.

There is a close relation between the size of needle, *i. e.*, the area of contacting point, etc., and the penetration. The needle used was a cylindrical steel one, having a diameter 1.445 mm. at 15° C., and a coefficient of linear expansion of 0.000009. The area of contacting surface of the needle changed with change in temperature. The contacting areas at 15° C. and −50° C. were 1.641 and 1.640 sq. mm., respectively.

Since the change of 0.001 sq. mm. was small in comparison with the total area, it was disregarded in tests between room temperature and −50° C.

Relation between Load and Penetration.—To test the precision of the apparatus, different loads were applied on the same sample and the relation between the load and penetration was determined. The sample was placed on the position S, cathetometer was adjusted to the D line, the load was applied and the reading was made after 30 seconds in the same way as before. The readings are expressed as

units of 1×10^{-2} mm. The thicknesses of samples I, II, III, and IV were 5.3, 5.6, 3.5, and 3.6 mm., respectively.

Figures 3 and 4 show the results. The relation is linear up to a penetration of 2.3 mm. (Fig. 3) and 2.0 mm. (Fig. 4), but the penetration is not proportional to the load above these points. Zimmerman and Brown[1] found that the maximum
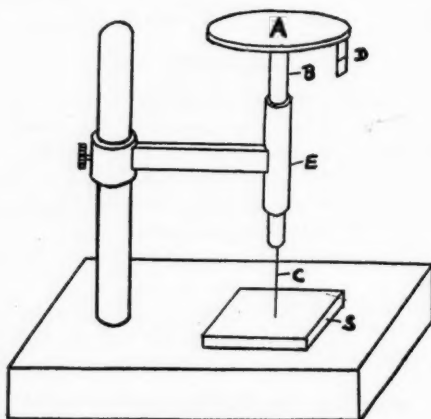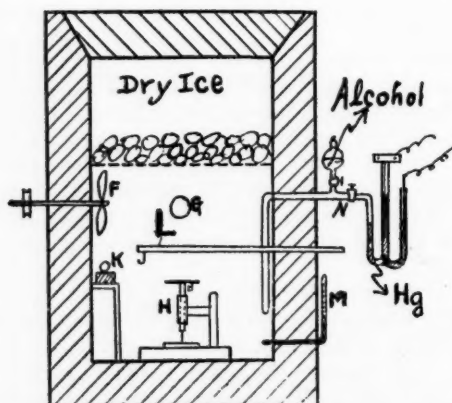

Figure 1

Figure 2—F, Agitator; G, Heater (Electric Bulb); H, Hardness Apparatus; K, Loads; L, Lever for Lifting Weight; M, Thermometer; N, Temperature Regulator

penetration was 2.50 mm. when the size of needle was 1.25 mm., with semicircular end; they recommended that the thickness of sample should be at least 12 mm. and is best at 25 mm. and comparisons should be made by using samples of the same thickness.

Obviously there is a close relationship between the thickness of sample and the penetration, but it may be unnecessary to use especially thick sheets if the maximum penetration is measured for each thickness. The author considered it satisfactory

to plot the maximum values as shown in Figs. 3 and 4.   The maximum penetration is 2.3 mm. for the sample 5.5 mm. thick and 2.0 mm. for the sample 3.5 mm. thick.

Figure 3

Figure 4
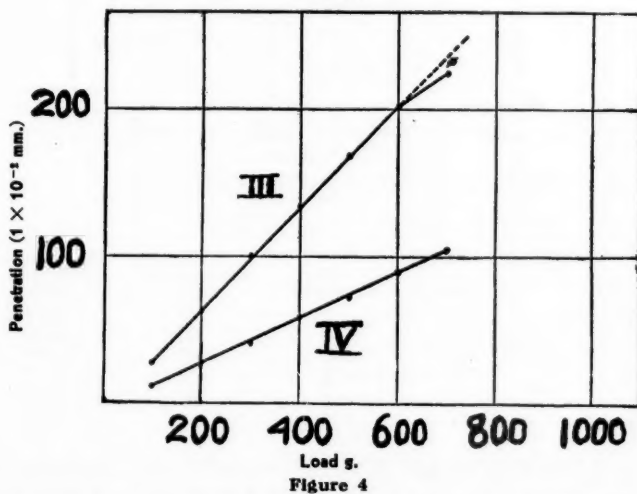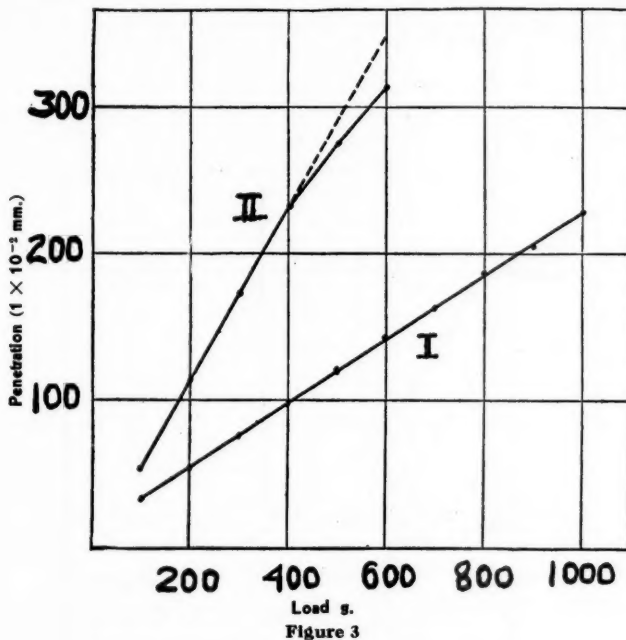
Relation between Penetration and Shore Hardness.—Samples of different hardnesses were tested in the new apparatus and by a Shore instrument to find the relation of penetration and Shore hardness.   The experimental results are shown in Fig. 5, in which curves are asymptotically related.

Gottschalk[2] estimated penetration with a sample 6 mm. thick, and found a linear relation between penetration and Pusey and Jones hardness.

Hardness of Rubber-Sulfur Vulcanizates at Low Temperatures

Vulcanizates of only rubber and sulfur were tested for hardness between room temperature and $-50°$ C. with the new apparatus.

They were vulcanized for different lengths of time in a press at a temperature corresponding to 50 lb. per sq. in. steam pressure.
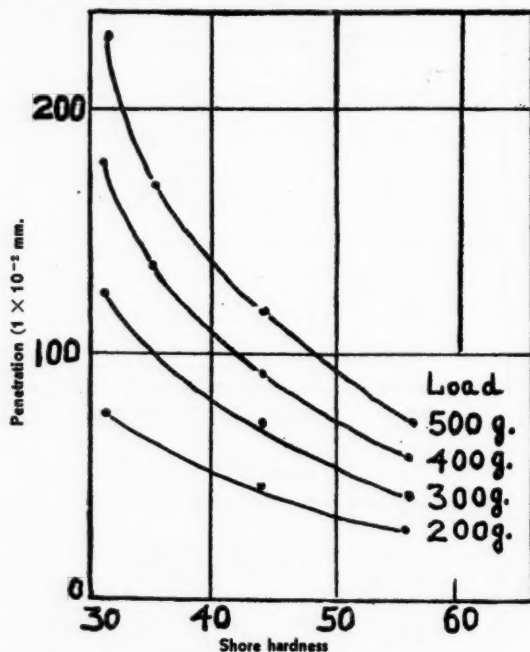

Figure 5—Relation between Penetration and Shore Hardness

TABLE I   COMPOUNDING

Sample	Raw Rubber (F. A. Q.) Percentage	Sulfur, Percentage	Time of Vulcanisation (Min.)	Thickness of Sample (Mm.)
R_2	98	2	120	3.27
R_5	95	5	90	3.63
R_{10}	90	10	60	3.97
R_A	95	5	60	5.16
R_B	95	5	90	5.17
R_C	95	5	120	5.23

Figures 6 and 7 show the results. Each curve showed hyperbola and increased its hardening ratio at $-45°$ C., then it was completely frozen hard at $-50°$ C.

An increase in sulfur content increased the hardness, as seen in Fig. 6, and when the total sulfur content was constant (Figs. 7 and 8) the hardness increased with increase in time of vulcanization. Since the maximum penetration on the R_2-curve of Fig. 6 exceeded 2.0 mm. and the maximum values in Fig. 7 exceeded 2.3

mm., the actual penetration seemed to be less than the true penetration. Figure 8 shows the result of using a 250-gram load and the state around room temperature.

Hardness of Rubber-Sulfur-Softener Vulcanizates at Low Temperatures

The hardness of vulcanized rubber containing softening agents, beside rubber and sulfur was measured over a wide temperature range.
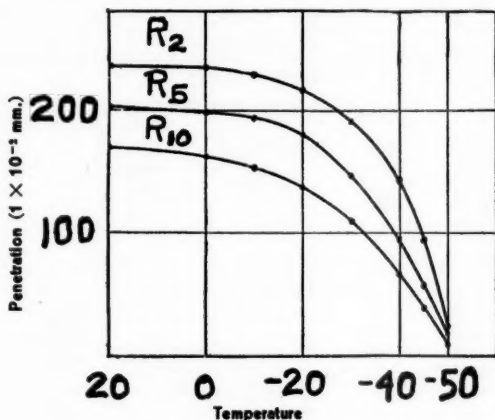

Figure 6

Figure 7

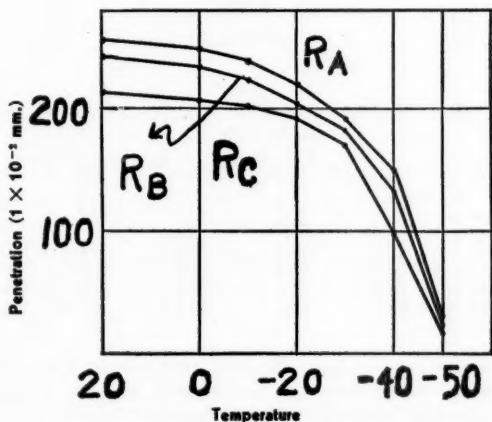*A. Addition of Softening Agents Having High Viscosities.*—The softening agents shown in Table VI were added to rubber-sulfur mixtures, and the new mixtures were vulcanized in steam at 50 lb. per sq. in. These samples showed the hardness values given in Table VII.

B. Addition of Softening Agents Having Low Viscosities.—Hardness of compoundings shown in Table IV are estimated as in A and are indicated in Table V.

TABLE II—COMPOUNDING

Sample	Rubber, Percentage	Sulfur, Percentage	Softening Agent	Time of Vulcanization (Min.)	Thickness of Sample (Mm.)
P	90	5	Liquid paraffin, 5%	90	5.12
M	90	5	Machine oil, 5%	90	4.93
C	90	5	Castor oil, 5%	90	5.03
V	90	5	Vaseline, 5%	90	5.09

TABLE III—RELATION BETWEEN TEMPERATURE AND PENETRATION
(LOAD 500 G.)

Sample	Penetration (1×10^{-2} Mm.)					
	0°	−10°	−20°	−30°	−40°	−50°
P	287	284	266	222	156	33
M	278	259	239	193	136	18
C	247	235	218	193	144	18
V	260	243	228	188	147	20

TABLE IV—COMPOUNDING

Sample	Rubber, Percentage	Sulfur, Percentage	Softening Agent	Time of Vulcanization, (Min.)	Thickness, (Mm.)
P_C	90	5	p-Thymol, 5%	90	5.40
T	90	5	Toluene, 5%	90	5.45
X	90	5	Xylene, 5%	90	5.45
D	90	5	Decalin, 5%	90	5.38
M_A	90	5	Methylaniline, 5%	90	5.05
E_A	90	5	Ethylaniline, 5%	90	5.45

TABLE V—RELATION BETWEEN TEMPERATURE AND PENETRATION
(LOAD 500 G.)

Sample	Penetration (1×10^{-2} Mm.)						
	0°	−10°	−20°	−30°	−40°	−45°	−50°
P_C		266	258	216	172	96	48
T	227	226	208	196	137	68	25
X	247	244	224	202	147	64	30
D	253	232	228	208	136	69	29
M_A	250	228	225	205	153	66	21
E_A	256	251	234	211	167	94	35

Softening agents belonging to A are fluids of high viscosity but these are solidified at −40° C. or below. Therefore, the vulcanized samples containing these substances do not show much softening effect at around −50° C.

Substances belonging to B have very low viscosity but low in freezing point and high in boiling point. These are believed to give softening effect at around −50° C. when the amount of addition is sufficient. Figure 9 indicates the result of 5 per cent softening agent; Curve P_C shows the result fairly well, but it cannot be said to be striking with 5 per cent addition. Accordingly, vulcanized rubber consists of raw rubber and sulfur is prepared, it is immersed in decalin until it reached a sufficient absorption and the hardness is estimated in order to find a clear result. The results are shown in Fig. 9.

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No comparative test can be made as each sample has different thickness, but the sample containing more than 30 per cent is much softer. However, it is well known that the use of large quantities of softening agents to increase softness at low temperatures makes rubber too soft at ordinary temperatures and diminishes its tensile strength.
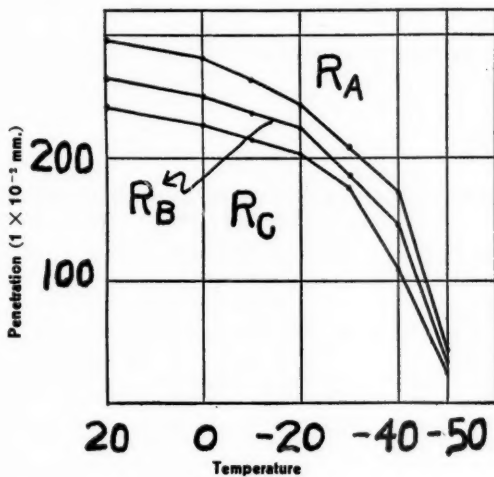

Figure 8
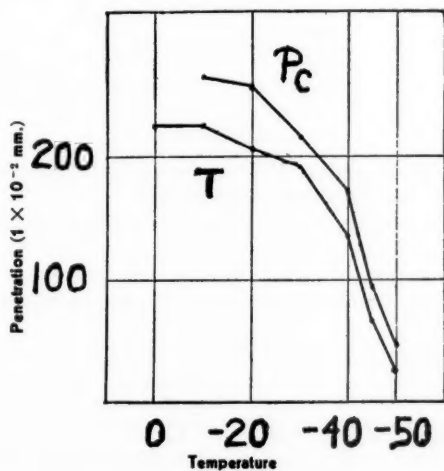

Figure 9

Hardness of Vulcanized Rubber Containing 30 Per Cent of Reclaimed Rubber at Low Temperature

Thirty parts of reclaimed rubber is added to the raw rubber and vulcanized as indicated in Table VI. The hardness is shown in Table VII.

TABLE VI—COMPOUNDING

Sample	Raw Rubber (Parts)	Reclaimed Rubber (Parts)	Sulfur (Parts)	Time of Vulcanisa-tion (Min.)	Temp. of Vulcani-sation (Lb. per Sq. In.)	Thick-ness of Sample (Mm.)
R-black	70	30	10	75	50	5.53
R-red	70	30	10	60	50	5.40

TABLE VII—HARDNESS (PENETRATION 1×10^{-2} WITH 500 G. LOAD)

Sample	Penetration $-40°$	$-45°$	$-50°$
R-black	115	70	22
R-red	136	77	24

Hardness at Low Temperature of Vulcanized Rubber Containing Di- and Trinitrobenzene

Compoundings, as indicated in Table VIII, with the use of di- and trinitrobenzene are made and vulcanized; the hardness is shown in Table XIV.

TABLE VIII—COMPOUNDING

Sample	Raw Rubber (Parts)	PbO (Parts)	$C_6H_4(NO_2)_2$ (Parts)	$C_6H_3(NO_2)_3$ (Parts)	Vulcanisation (Min.)	(Lb. per Sq. In.)	Thick-ness (Mm.)
D.N.B.	200	30	10	0.0	30	50	5.06
T.N.B.	200	30	0.0	10	40	50	4.98

TABLE IX—HARDNESS (PENETRATION 1×10^{-2} MM. WITH 500 G. LOAD)

Sample	Penetration $-40°$	$-45°$	$-50°$
D.N.B.	130	70	16
T.N.B.	108	64	11

Conclusions

1. By means of a new apparatus which is described, it is possible to estimate the hardness of vulcanized rubber at low temperatures.

2. The hardness of rubber-sulfur vulcanizates increases hyperbolically with lowering of temperature and they become "frozen" and hard at $-50°$ C.

3. Since ordinary softening agents having high viscosities solidify at $-30°$ to $-40°$ C., these are unsuitable for softening rubber to be exposed to temperatures below this range.

4. Softening agents which do not solidify at $-50°$ C. are among those ordinarily used as solvents, and they have very low viscosities. Though their effect on the hardness of rubber at $-50°$ C. is small when they are used in small percentages, they prevent the freezing of rubber at $-50°$ C. when large proportions are used. They are, however, of no practical value, since they decrease the tensile strength of rubber.

5. Vulcanized rubber containing 30 per cent of reclaimed rubber also froze to a hard product at $-50°$ C.

6. The relation between temperature and hardness of rubber vulcanized with organic accelerators is the same as that in the case of rubber vulcanized with sulfur alone.

Thanks are due to Dr. H. Inoue, head of the Fifth Department of this laboratory for his kind advice.

References

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Properties of Hard Rubber

I. Plastic Deformation

H. F. Church and H. A. Daynes

INTRODUCTION

The plastic flow of hard rubber under load is a property which merits serious attention, in the first place as a criterion of cure and in the second because of its importance in most industrial applications where change of shape under load cannot be tolerated.   Change of shape is accelerated by elevated temperature to such an extent that under tropical conditions hard rubber is unsuitable for certain uses for which it would otherwise be the ideal dielectric.   The effect of temperature upon flow must therefore be studied with a view to improving the material by raising its permissible working temperature, and it becomes necessary to decide upon a suitable method of test.

Certain control tests of plastic yield with temperature are used commercially in judging the suitability of solid dielectrics for various purposes, and there is a growing tendency for a test of the Marten type to be adopted.   In this test a known uniform stress is applied by four-point loading to a strip of the material 120 x 15 x 10 mm.   The whole apparatus is in a heating chamber, which can be raised in temperature at a steady rate of 50° C. per hour, and the yield of the sample is continuously observed.   The temperature of the heating chamber when the yield has reached a certain pre-determined value is used to denote the grade temperature of the material.   This test is considered to be of doubtful value for research purposes, since the results are dependent on a number of arbitrary conditions and therefore do not represent an intrinsic property of the material.   For instance, it has been stated that the temperature of the specimen lags some 5° or 6° C. behind that of the heating chamber.   Moreover, it is to be expected that the interior of the sample will be at a different temperature from that of the surface, so that a material of high thermal diffusivity will be handicapped.   It was therefore decided to devise a test in which the temperature of the specimen is either kept constant, or varied under such conditions that the temperature is known and reasonably uniform; also to search for some simple plastic property of the material, the temperature curve of which shows an easily recognizable singularity at a temperature independent of arbitrary experimental conditions.   A twisting stress on a strip 1 mm. thick was chosen for preliminary tests.   This lends itself to a compact design of apparatus, in which rapid and uniform heating may be secured if necessary by immersion in a liquid; also the stress is uniform throughout the length of the specimen and the resulting distortion is easily measured.   The apparatus and methods described in this report represent an early stage in the exploration of the possibilities of such a test, and no recommendation is made at present as to their use for specification purposes, but in the course of development information has been obtained as to the nature of the plastic flow of hard rubber which appears to be of sufficient interest to warrant publication.

EXPERIMENTAL

Twisting tests were made at temperatures varying from 15° to 100° C. on strips of the material 50 x 10 x 1 mm. Two types of test were made: (A) measurement of set after subjection for a definite period to a fixed torsional strain; and (B)

(a)

SET-TEMPERATURE CURVES FOR PHYSICAL MODEL
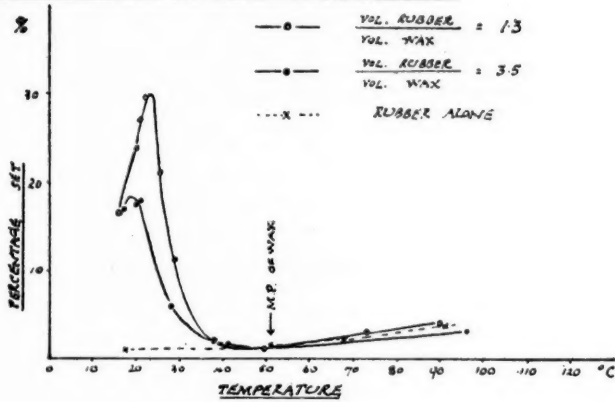
(b)

SET-TEMPERATURE CURVES FOR MATHEMATICAL MODEL

$$x = \frac{4}{5}\left(1 - e^{-0.0005 e^{0.11t}}\right) e^{-0.0001 e^{0.11t}} \times 100$$
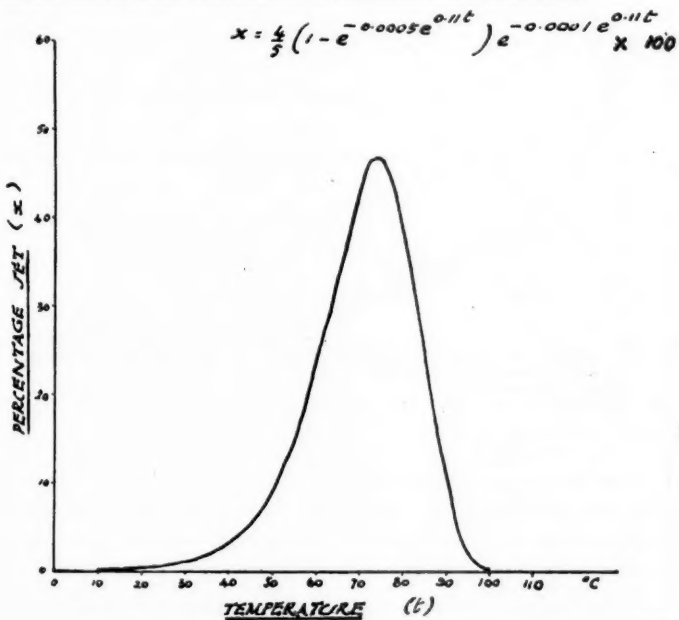
Figure 1

measurement of rate of yield under a torsional stress which produces a fixed initial strain.

Sub-Permanent Set

Method of Test.—The apparatus devised is illustrated in Fig. 5 (*a*). The hard
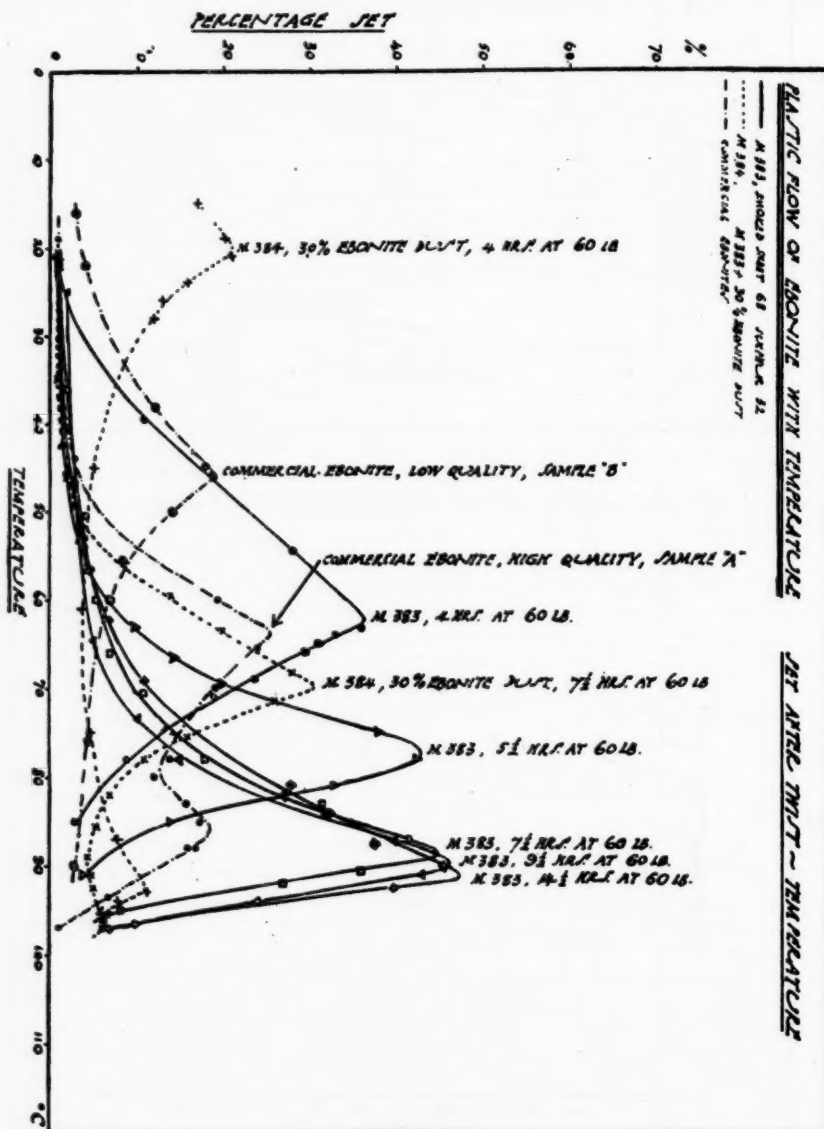

Figure 2

rubber strip *E* was clamped at the lower end to a fixed base *B*, and on the upper end was clamped a rigid pointer *P* which, on rotation, moved over a horizontal

circular scale S graduated in degrees. The center of the pointer was attached to a taut vertical cotton thread F, which served to support the pointer and attachments when the ebonite had become plastic and would otherwise have collapsed under load. Preliminary tests showed that the thread exerted no appreciable torsional stress on the specimen. The required twist was applied by means of a forked member A which could slide vertically in a collar C and which could be fixed in position by a screw N. The apparatus was immersed in water to cover the hard rubber, but not the scale, the water being maintained at the desired temperature.

At each of a series of temperatures the sample was kept twisted through about 20 degrees of arc for a period of one minute, readings of the twist being taken at both ends of the pointer. The sample was then released and readings were taken at intervals of 15 seconds, 1 minute, 2 minutes, and 3 minutes after release. In the appended curves, Fig. 2, the 2-minute reading is plotted. The recovery was not instantaneous, but after 2 minutes the time-set curve was showing distinct signs of flattening. The residual deflection after 2 minutes was expressed as a percentage of the twist applied, and was called "percentage set." After each test, while the temperature was being adjusted to a new value, the pointer was twisted in the reverse direction to recover the original zero approximately, and during the next test measurements were made relative to the new zero.

Samples Tested.—The following samples were tested: M. 383. Smoked sheet 68, sulfur, 32 parts by weight. Vulcanized 4, $5^1/_2$, $7^1/_2$, $9^1/_2$, and $14^1/_2$ hours at 60 lb. per sq. in. steam pressure. M. 384. M. 383 stock 100, ebonite dust from a pure hard rubber 30 parts by weight. Vulcanized 4 and $7^1/_4$ hours at 60 lb. per sq. in. A. Commercial hard rubber of good quality. B. Commercial hard rubber of low quality. The available analytical data for these mixings are given in Table I.

<div align="center">TABLE I</div>

Sample	Specific Gravity	Ash at 650° C. (Percentage)	Organic Acetone Extract (Percentage)	Free Sulfur (Percentage)	Total Sulfur (Percentage)	Combined Sulfur (Percentage)	Vulcanization Coefficient
M. 383. $5^1/_2$ hr. vulcanization	...	(0.16)	1.47	2.72	(31.94)	(29.22)	43.15
M. 383. $7^1/_2$ hr. vulcanization	...	0.16	1.48	1.99	31.94	29.95	45.16
M. 383. $14^1/_2$ hr. vulcanization	...	(0.16)	1.79	1.57	(31.94)	(30.37)	45.93
A.	1.175	1.09	1.23	2.12	32.5	30.4	46.5
B.	1.389	23.5	4.96	0.78	18.1	17.3	...

Results of Set Tests.—The data obtained in these tests are plotted in Fig. 2, the following being the principal conclusions:

(a) With rise of temperature the material in general became at first more plastic and later returned to a highly elastic condition, the set showing a sharp maximum at a temperature depending on the type and cure of the material. In the elastic state at high temperatures the rigidity was comparatively small, the rubber being incapable of supporting the weight of the pointer. The relation between temperature and set was completely reversible, the same results being obtained on repeating the tests in any order; the form of the curve was therefore not attributable to any permanent change in properties caused by heating or twisting.

(b) The temperature at which the peak occurred increased progressively with vulcanization, and with M. 383 appeared to approach a limit at a little above 90° C.; prolonging the cure beyond $7^1/_2$ hours had very little effect. It is interesting to note that, according to the data in Table I, the sample with $7^1/_2$ hour cure had a vul-

canization coefficient near to the value (47.1) corresponding to the compound C_5H_8S, and the rate of combination was greatly reduced.

(c) The set at the peak temperature increased somewhat with vulcanization, the difference between samples vulcanized from $7^1/_2$ to $14^1/_2$ hours again being small.

(d) The sharpness of the maximum increased with vulcanization, except that at the higher temperatures there were indications of decreasing sharpness on the low temperature side. The maximum was in most cases sufficiently sharp to define the peak temperature within about $\pm1°$ C.

(e) The relationship between permanent set and vulcanization for M. 383 at a series of temperatures is shown in Fig. 5 (a) which has been constructed from data obtainable from Fig. 2. Again $7^1/_2$ hours' vulcanization was a dividing line between a condition in which the set was comparatively independent of cure and one in which sharp maxima occurred. The maximum moved in the direction of longer cure as the temperature rose, but was masked at the highest temperatures by the high set at advanced vulcanization. The vulcanization-set curve at, say, 75° C. might be a useful basis for defining state of cure.

(f) The introduction of hard rubber dust into the mixing depressed the peak temperature. It will be seen from Fig. 2 that 30 per cent of added dust lowered the peak temperature from 87.5° to 70° C. in the $7^1/_2$ hour cure and from 62° to 20° C. in the 4 hour cure (Cf. M. 383 and M. 384). In this sense the dust produced the same effect as a retardation of vulcanization, but, as will be seen later, the peak temperature is a complex property, so that retardation of vulcanization is not the only possible explanation of the effect. Addition of dust lowered also the magnitude of the set at the peak temperature.

(g) The inclusion of dust introduced a second peak at a higher temperature than the main peak (see curves for M. 384, 4 and $7^1/_2$ hour vulcanizates), and this second peak, like the main peak, moved in the direction of higher temperature as the vulcanization advanced. The shapes of the temperature-set curves for the dust mixings were not simply the result of superposing the curves which would have been obtained for homogeneous hard rubbers having the same compositions and times of vulcanization as the once-vulcanized and twice-vulcanized components. The general shape and the effect of increasing cure on the positions of the peaks were the same as the superposed curves of the type suggested, but the peak temperatures were not obviously related to those of the separate components.

(h) The high quality commercial sample which, no doubt, contained dust, showed two peaks, the main peak temperature being 64° C., little higher than that of the dust-free mixing M. 383 at 4 hours' vulcanization. The fact that these two samples have nearly the same peak temperatures but distinctly different average percentages of combined sulfur suggests that the effect of dust in lowering the peak temperature is not merely, if at all, due to a retardation of vulcanization.

(i) The low quality commercial sample B showed only one peak, but it is not improbable that it consisted mainly of dust.

Effects of Some Experimental Conditions.—A marked peak temperature having been found for each material under fixed conditions, it was next determined whether this temperature was characteristic of the material or was affected by variations in arbitrary conditions of test.

(i) *Effect of Duration of Torque* (T_1) *and Interval after Release* (T_2).—Previous tests had been made with the sample 1 minute under torque and released for 2 minutes before measurement. Temperature-set curves were next determined on a further sample of M. 383, 4 hours' vulcanization, under the following conditions:

$T_1 = 1$ min., $T_2 = 2$ min. (Curve 1).
$T_1 = 1$ min., $T_2 = 15$ sec. (Curve 2).
$T_1 = 10$ min., $T_2 = 2$ min. (Curve 3).
$T_1 = 10$ min., $T_2 = 15$ sec. (Curve 4).

The results are plotted in Fig. 5 (b), and show that there is little if any alteration in the peak temperature, though the shapes of the curves vary somewhat. The set maximum increases with an increase in T_1 or a decrease in T_2 as would be expected.

(ii) *Thickness of Specimen.*—For comparison with Curves 1 and 2, for which a standard sample of 1 mm. thickness was used, curves were obtained under similar conditions with a second sample of 3 mm. thickness. A comparison of Curves 1 and 5, and 2 and 6, respectively, in Fig. 5 (b) shows that the thickness has little effect on the height of the peak, the peak temperature, or the general shape of the curve.

(iii) *Twist per Unit Length of Specimen.*—Two samples of M. 383, vulcanized $9^{1}/_{2}$ hours, were tested at 10° and 20° twist, respectively. The curves for the two samples could not be distinguished from one another and are shown as one, Curve 7 in Fig. 5 (b). Curve 8 represents the results for a similar pair of tests made with a shorter period of recovery (15 sec.), the curves for the two twists being indistinguishable.

Discussion of Results.—In a preliminary report of this kind a full discussion of results, some of which clearly require amplification by further experiment, is not possible. Some practical considerations may, however, be pointed out.

(a) If it is considered that the suitability of a material for practical purposes may be judged, among other considerations, by its set after a given torsional strain, then it is not sufficient to make a test only at the maximum temperature to which it may be subjected during use. The temperature-set curve is usually such that the set at the upper limit of temperature may be exceeded at some lower temperatures.

(b) It is sometimes alleged that hard rubber in panel form shrinks under tropical conditions to an extent which cannot be explained by reduction of volume due to loss of volatile components such as water. It has been shown in these experiments that early during vulcanization hard rubber acquires an elastic structure, which exerts a restoring force when the mass is deformed. Although it may be masked by the more rigid plastic structure at low temperatures, this restoring force takes control again on reheating to a sufficiently high temperature. This latent elasticity may be sufficient to account for the alleged shrinkage if in manufacture the sheet has been allowed to flow under pressure and then cooled too rapidly for elastic recovery to take place. The effect appears to be parallel to the shrinkage of calendered unvulcanized rubber and of racked rubber. The latent elasticity was shown to be permanent by the following experiments, which served also as a visual demonstration of the property.

A sample of undervulcanized hard rubber containing hard rubber dust (M. 384, 4 hours' vulcanization) and having a peak temperature of 20° C. was easily bent and twisted in the hand at room temperature and showed little tendency to return to its original shape. When warmed in water at 50° C. it rapidly became straight and appeared elastic though very flexible. When bent in warm water and transferred, still bent, to cold water it hardened in the bent position, but became straight again on reimmersion in warm water. The same sample was later hardened in a twisted form and left for 3 weeks. On warming, it immediately straightened itself, showing that the latent elasticity was not rapidly fugitive.

Another sample (rubber 68, sulfur 32, vulcanized 6 hours at 60 lb. per sq. in.) was given a preliminary molding vulcanization which imparted only a rough

finish. The vulcanization was then completed under mechanical pressure between plates of glass, which gave a smooth finish. A long rectangular slip was cut from this and measured before and after heating for an hour at 90–100° C. The heating caused changes in the length, breadth, and thickness of −1.5, −4.0, and 5.4 per cent, respectively. The sides of the strip became curved, and the general effect of the heating was to restore the first rough finish. Another sample vulcanized at a lower temperature and under lower mechanical pressure introduced at an earlier stage of cure showed a lower shrinkage on heating.

Shrinkage tests were carried out on commercial samples supplied by five manufacturers. In all cases there was marked shrinkage, although only one sample was less than 4 years old and one was 7 years old. The pressure conditions, facilities for flow during vulcanization, and temperature cycle, especially towards the end of vulcanization and during cooling, are evidently of great importance in avoiding subsequent shrinkage.

(c) If the existence of two peak temperatures is eventually proved to be characteristic of hard rubbers containing dust, a temperature-set curve will form a test for the presence of dust, and possibly of the amount of dust and its state of vulcanization.

(d) The behavior of hard rubber in these experiments gives promise of throwing light on the nature of the plastic flow, on the changes in structure which take place during vulcanization, and on the functions of hard rubber dust as a compounding ingredient. A working hypothesis which describes the main features of the observed phenomena is discussed in the next section.

Elastic Structure of Hard Rubber.—In the experiments described hard rubber behaves as if it consists of two components, one elastic and dominant at high temperatures and the other plastic and dominant at low temperatures. The main features of the temperature-set curves may be explained by supposing that the plastic phase "melts" (or softens), losing its frictional properties, and simultaneously becomes less viscous with rise in temperature. Such a structure may be represented diagrammatically by the system shown in Fig. 5 (b), where E_1 and E_2 are elastic springs and P is a piston moving in a medium possessing both frictional and viscous properties of which one or both decrease with temperature. During a fixed extension of the system the piston would be drawn out to an extent depending on the strength of spring E_2 and the nature of the medium. On release the system would recover immediately to an extent depending on the relative strengths of springs E_1 and E_2 and the extent of flow during the period of extension. It would then creep back exponentially with time to a final position depending on the ratio between the friction constant of the medium and the strength of E_1. The time constant of the creep would depend on the strengths of E_1 and E_2 and the mobility of the medium. E_1 represents the elastic component of hard rubber and the combination of E_2 and P the plastic component. A somewhat similar model has been used by Healey (*India-Rubber J.*, **69**, 57 (1925)) to illustrate the behavior of raw and soft vulcanized rubber.

The general equation for the set of such a model has been derived in terms of the strengths of the springs, the frictional and mobility coefficients of the medium, and the times of extension and recovery, but as the values of the various constants and their variations with temperature have not been investigated, it is premature to discuss the theory in detail. It is of interest, however, to compare the set curve in Fig. 2 for M. 383, vulcanized $5^1/_2$ hours, with the theoretical curve in Fig. 3 (b), which has been calculated on a basis of some plausible assumptions to show that a curve of the right type is produced. Experimental confirmation will be attempted as opportunity occurs.

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Temperature
Figure 3
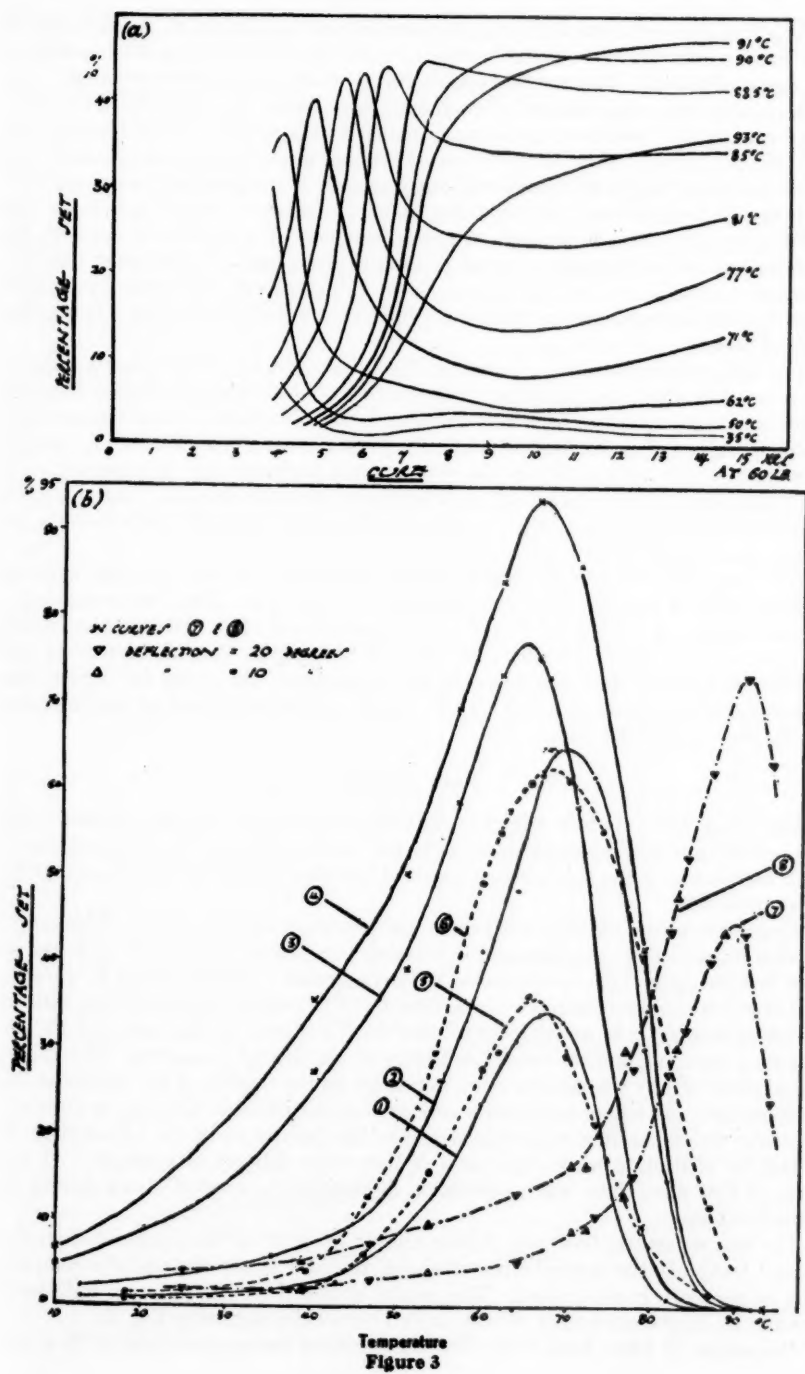
Experiments were carried out with a model which was known to possess some of the features assumed in the foregoing theory to demonstrate the type of temperature-set curve obtained. This model consisted of a short piece of rubber tubing filled with paraffin wax, and clamped at each end, thus sealing the wax within the tube. The twisting test described above was applied to the model. A preliminary test with the rubber tube alone showed that soft rubber did not behave in the same way as ebonite over the range considered, but increased in set gradually and uniformly with rise in temperature, the set being at no temperature comparable with that obtained at the peak temperature with hard rubber. (The increase in set with rise of temperature is contrary to what is usually observed with set after constant elongation at ordinary testing temperatures; this apparent discrepancy may arise from the higher temperature range and different method of applying stress in the present tests.)

The temperature-set curve, shown in Fig. 3 (a), was similar in general shape to curves obtained with hard rubber. As in the case of hard rubber, variation of period of recovery before measuring the set did not appreciably affect the peak temperature. An increase in the elastic control relative to plastic control was obtained by using a rubber tube of smaller bore but the same outside diameter and, as expected, both the peak temperature and set at peak temperature were reduced. By analogy it may be inferred that the effect of long vulcanization in hard rubber is to make the plastic factor more dominant.

It is important to observe that the peak temperature is not identical with the melting point of the wax, but occurs some 30° C. below it. The peak temperature therefore does not correspond to a phase change in the plastic; in fact at the melting point of the wax the set of the model is no different from that of the rubber tube alone. By analogy the convergence of the temperature-set curves for hard rubber towards a temperature of about 97° C. would suggest some sort of melting point of the plastic at that temperature.

Rate of Flow

Method of Test.—It was originally intended to measure the rate of flow under the application of a constant stress as in the usual cantilever bending test, but at high temperatures the thin strip of hard rubber was so flexible that the apparatus was unsuitable.

Tests were therefore tried with the apparatus shown in Fig. 5 (c). The sample E with its pointer P was clamped in relation to a horizontal scale S as in the set test, but the upper end was connected to the inner end of a spiral spring T, the outer end of which could be rotated by a member H. The pointer was set at zero with the spring unstrained. M was quickly rotated until the pointer was deflected 10° and was then clamped, and the rate of deflection of the pointer measured. The applied initial stress at any temperature thus depended on the rigidity of the rubber at that temperature. At higher temperatures there was considerable difficulty in obtaining accurate results, as flow commenced before the pointer could be adjusted to the initial 10° deflection while high rates of flow were difficult to measure. At high rates of flow also, there was appreciable diminution in applied stress during the period of test.

The test measures, however, a more simple property of the material than does the set test since the applied stress does not diminish as rapidly, and the complication of recovery is eliminated. The results obtained on M. 383 were sufficiently definite to show some points of interest and have been plotted in Fig. 4.

Discussion of Flow Tests.—(a) The temperature for a given rate of flow rises

with increasing vulcanization, but does not change much beyond $7^1/_2$ hours. This is similar to the temperature for a given set.

PLASTIC FLOW OF EBONITE WITH TEMPERATURE
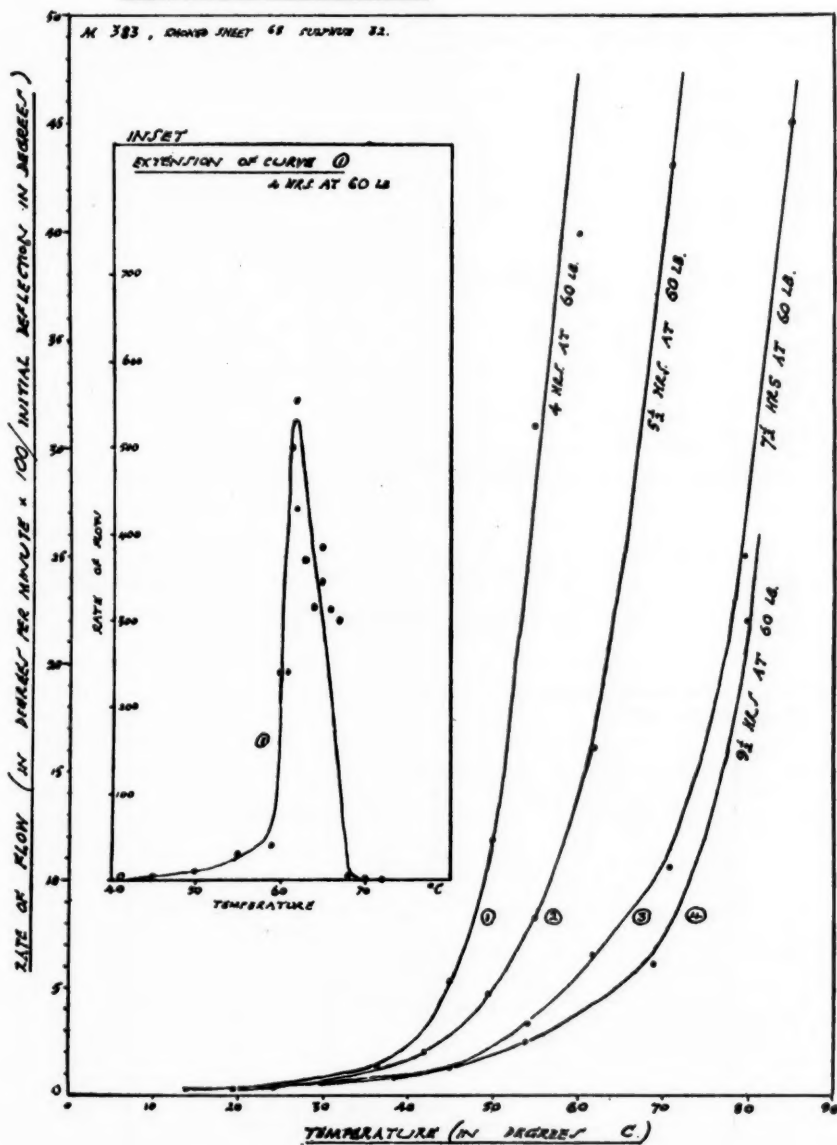
RATE OF FLOW ~ TEMPERATURE

Figure 4

(b) In the only case (the 4 hours' vulcanization) where tests were taken to a sufficiently high temperature there was a sharp maximum in rate of flow at about
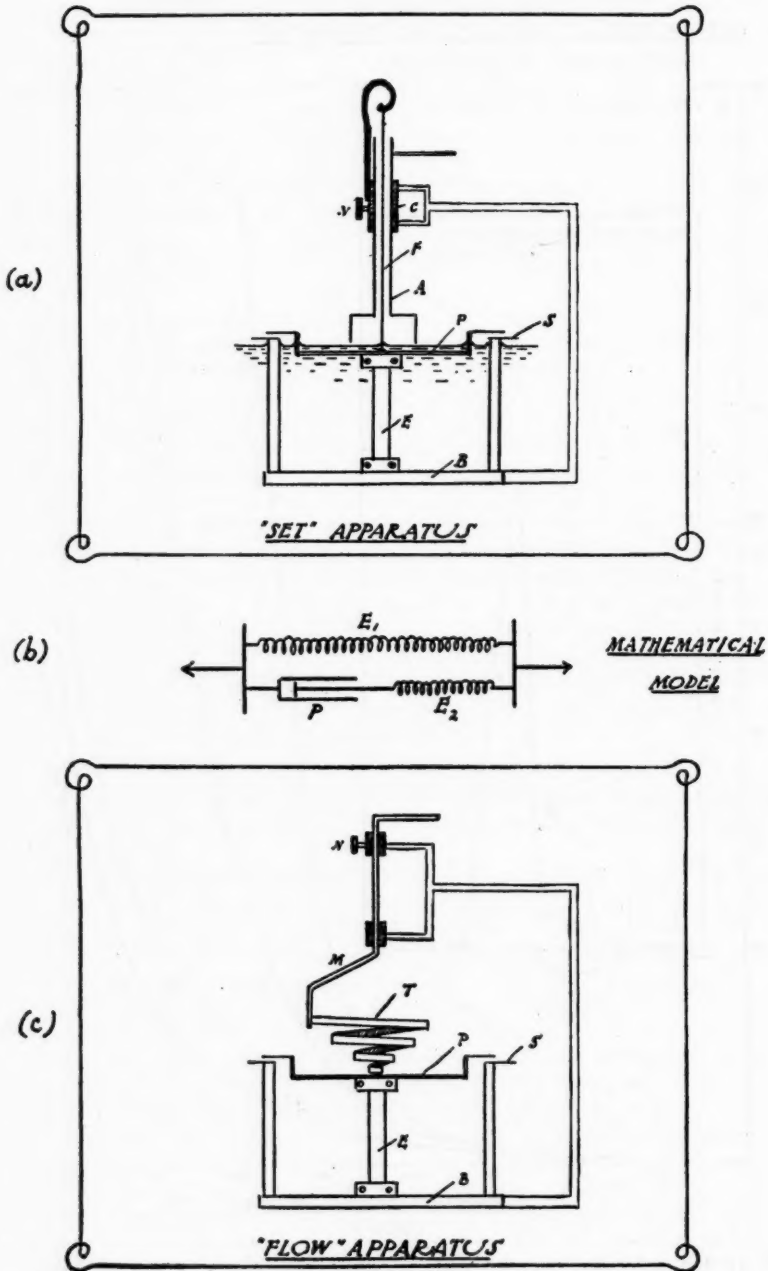
PLASTIC FLOW OF EBONITE WITH TEMPERATURE

(a)

"SET" APPARATUS

(b)   MATHEMATICAL MODEL

(c)

"FLOW" APPARATUS

Figure 5

62° C., the same as the peak temperature in the set test. On the low temperature side the rate of flow increased tenfold per 3° C.; on the high temperature side the flow became negligible in a further 6° C. The sharpness of the peak leads to two considerations of practical importance.

(i) It is misleading to compare two materials by their rates of flow under specified loads except under the strictest conditions of temperature equality.

(ii) The principle of defining the grade temperature of a material by the temperature at which the total yield of a specimen reaches a predetermined point when heated at a given rate is sound in the sense that most of the yield takes place in a very narrow margin of temperature. On the other hand it is the more necessary that the temperature should be uniform throughout the specimen. A small fraction of material at a lower temperature in the center may exert the major part of the elastic control. It would be better from this point of view to measure the temperature at which rigidity reappears on cooling rather than that at which flow occurs on heating.

SUMMARY

Tests have been made at temperatures from about 15° to 100° C. on (a) sub-permanent set due to torsion; and (b) rate of plastic flow under torsion, of a number of commercial and specially made hard rubbers, the latter consisting of rubber and sulfur with or without high grade hard rubber dust.

Temperature-set curves showed marked maxima at temperatures, depending mainly on the vulcanization of the sample and comparatively little on arbitrary conditions of test. The peak temperature rose with advancing vulcanization, but reached a limit when combination of sulfur had practically ceased. Hard rubber dust depressed the peak temperature and introduced a second peak at a higher temperature, both peak temperatures rising with advancing vulcanization.

Vulcanization-set curves also showed sharp maxima except at the highest temperatures, but became flat when combination of sulfur had practically ceased.

Rate of flow under a torsional stress sufficient to give a fixed initial twist showed substantially the same characteristics as the set after torsion.

It is concluded that at an early stage in vulcanization hard rubber acquires an elastic structure which becomes the dominant control at high temperatures, the plastic structure being dominant at low temperatures.

Some practical consequences of these results are discussed, relating to testing of materials for plastic deformation, methods of manufacture to avoid after-shrinkage, detection of hard rubber dust, and investigation of changes of structure during vulcanization.

The Viscosity Characteristics of Rubber Solutions

W. Philippoff

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As is well known, solutions of rubber in organic solvents exhibit a variety of noteworthy properties which are characteristic of solutions of lyophilic colloids, to which rubber belongs. These properties, notably high viscosity even in dilute solution and structure viscosity, distinguish these solutions from those of normal substances of low molecular weights.

In the present article, the attempt is made to assemble known facts about viscosity phenomena and at the same time to add certain experimental data, heretofore unpublished, to the available literature on the subject.

Historical Survey

Viscosity measurements were employed for the first time, though in a purely qualitative way, by Axelrod[1] in 1904 as a means of judging the properties of rubber. He tried to draw conclusions from the diminution in viscosity during vulcanization, and also to characterize various types of rubber on a basis of the different viscosities of their solutions, *viz.*, that a high viscosity is evidence of high tensile strength. However, as remarked by Schidrowitz and Goldsborough,[2] the experiments of Axelrod do not justify his sweeping conclusions, for the experimental method was very defective. The much better executed experiments of Schidrowitz and Goldsborough represent the first viscosity measurements of rubber solutions which have in any way a quantitative significance. Among the first to carry out viscosity measurements were also Beam,[3] Henri,[4] Woudstra,[5] and Spence.[6]

In 1913 Fol[7] made a critical survey of the status of viscosity measurements up to that time, and added measurements of his own. He carried out extensive measurements on solutions of various concentrations and, as a means of characterizing various types of rubber, introduced the concept of *viscosity number*. This latter was used for a long time at the Netherlands Rubber Institute. Bernstein[8] studied the influence of milling, of "heat degradation," and of vulcanization on the viscosity.

It is significant that all these investigators, commencing with Axelrod, believed that there is a parallelism between the viscosity of rubber solutions and the degree of polymerization of the rubber, and they all concluded that a diminution in viscosity brought about by the various influences is an indication of depolymerization. The nature of this relation was, however, not investigated further.

Later in 1914, Kirchhof[9] studied changes in viscosity on addition of sulfur and as a result of thermal degradation. In this same year followed an exhaustive investigation of the influence of solvents,[10] which led to the discovery of the phenomenon later to be known as *structure viscosity*, *i. e.*, a diminution in viscosity in the Ubbelohde viscometer with increasing pressure. It had already been observed by Fol[7] that the relative viscosity (see below) depended on the particular viscometer employed, and he therefore emphasized the necessity of measurements with an accepted standard viscometer.

The measurements of Kirchhof may be regarded as the first on the structure viscosity of rubber solutions. In 1918 van Rossem[11] published a comprehensive

review of viscosity investigations which had been carried out at the Netherlands Government Rubber Institute during the years 1912 to 1916. In these investigations, the influences of concentration, agitation, light, moisture, solvent, resins, sulfur, etc., on the viscosity of rubber solutions, and also of the relation of the viscosity to the tensile strength and extensibility, were studied so thoroughly that the work has shed considerable light on the whole problem. Only the question of the effect of temperature, already studied by Fol, remained unsettled. Even the influence of acids and of atmospheric oxygen was studied.

From a qualitative point of view, these investigations gave a comprehensive idea of viscosity phenomena, but the structure viscosity which was observed by Kirchhof and which is influenced in uncontrollable ways by factors, such as temperature, was not worked out on a quantitative basis. These earlier investigations were a guide to further work on viscosity phenomena, and only the most important of this later work need be mentioned here.

In 1924 Herschel and Bulkley in the United States Bureau of Standards carried out their well-known investigations of the flowing of rubber solutions through capillaries, as a result of which the structure viscosity described by Kirchhof was substantiated. These very carefully executed measurements remained for a long time the most precise measurements of the flow of structurally viscous substances.[12]

In the following year Abernethy[13] carried out measurements of the relation between the temperature and the viscosity of very concentrated solutions of dead-milled rubber by the falling-ball method. Later in 1928 Fikentscher[14] made precise measurements of the influence of mastication on the concentration relations of rubber solutions. He likewise studied solutions of chlorinated rubber.

Kroepelin[15] in 1929 was the first to show how to express the results of measurements of substances exhibiting structural viscosity on a basis independent of the apparatus employed. In this work particular attention was devoted to rubber solutions. This method was employed by Staudinger[16] in his numerous measurements. Since 1922 Staudinger[17] has in a large number of works expounded his ideas on chain molecules and on the proportionality of the viscosity η_{sp}/C in dilute solutions and the molecular weight (this is discussed in detail later). He studied the part played by concentration and temperature on the properties of various types of raw and degraded rubber.

Stamberger and Blow[18] studied the influence of storage on the viscosity of masticated rubber, and proved that the viscosities of solutions prepared immediately after mastication are lower than the viscosities of solutions prepared from the same rubber which after mastication has been stored one or two weeks before solution. Dogadkin and Pewsner[19] have studied the structure viscosity of rubber solutions, particularly the changes in the relation between pressure and viscosity as a function of the extent of mastication. Haller,[20] Dogadkin and Lawrenenko,[21] and also Busse and Karrer[22] have investigated the relations between the viscosity and temperature of rubber solutions, and have found an apparent contradiction in the fact that the temperature coefficient can be positive, negative, or nil, in part at least because of inherent differences in various types of rubber. Nevertheless the temperature coefficient of the relative viscosity of rubber solutions is very small compared with that of other colloids, e. g., cellulose derivatives.

Structure viscosity, particularly in its theoretical aspects, and in its changes over a wide range, have been studied by Reiner[23] and by Reiner and Schoenfeld-Reiner.[24] These investigations have, with the aid of the theory of flow of anomalous liquids advanced by Reiner (also developed by Weissenberg[26]), firmly established the theoretical principles which govern the phenomenon. Finally Scheiber and Baier[27] have made a detailed study of the viscosity of chlorinated rubber.

Problems Connected with Viscosity Measurements

This historical survey makes evident the problem which is involved in viscosity measurements, *viz.*, to characterize a particular type of rubber under investigation by a few simple viscosity measurements. To settle this problem in a satisfactory manner, the way in which the measured viscosity depends on all the various influences must be known as precisely as possible. After these relations are known, the viscosity measurements which represent directly the behavior of rubber and do not depend on extraneous experimental conditions are selected as a criterion of the rubber. These various influences are discussed in detail elsewhere, and are also dealt with to a certain extent by Staudinger in his book,[16] but in the latter case, measurements of structure viscosity and of concentrated rubber solutions are very incomplete.

The method followed involves the exact definition of the viscosity of structurally viscous substances in the sense used by Reiner[25] and Weissenberg[26] for characterizing a substance by the *flow curve*, the apparatus for determining these curves, and in turn for defining in a theoretically exact manner the properties of a solution.

By means of empirical concentration factors, these properties of a solution can now be derived independently of the influence of the concentrations actually used. Measurements of the influence of temperature and of solvent then make it possible to eliminate further the influence of experimental conditions. When this is done, the effects of atmospheric oxygen and of acids can be studied. Frequently these are only correction factors.

This leads finally to the fundamental problem, *viz.*, the way in which the viscosity varies, independent of experimental conditions, with the extent of mastication, with the degree of vulcanization, and with the nature of the rubber. With these brief remarks as an introduction, a more thorough survey of the literature will be made.

Description of the Properties of Solutions

In the following section, the mathematical features of structure viscosity are reviewed as they appear in the works of Reiner[25] and of Weissenberg,[26] and as they have already been reviewed in detail several times before by the present author.[28]

As is well known, liquids, in contrast to rigid substances, exhibit the phenomenon of flow, and under the influence of the smallest external force they change their form. This deformation in true liquids occurring in nature involves an expenditure of energy to overcome friction in the liquid. As is also known, in the flow of liquids through tubes, there are two types of flow, laminar and turbulent. In the first case, which is found experimentally only with slow flow, the liquid moves in layers sliding on one another, so that the hydrodynamic relations involve only relatively simple calculations. Turbulent flow, which appears only after a definite critical rate of flow is attained, is the result of irregularly distributed vortex movements which eddy through the layers of the laminar current and lead to a uniform average rate of flow over the cross section of the tube.

In general with normal liquids, η is constant with laminar flow, whereas with turbulent flow the viscosity, calculated by the same law as for laminar flow, apparently increases. This increase of the apparent viscosity upon transition from laminar to turbulent flow is a characteristic and easily recognizable phenomenon which serves to distinguish the two types of flow.

According to the Newton hypothesis, which has been proved experimentally to hold true of normal liquids or Newtonian liquids, the frictional force between two

layers in laminar flow, based on 1 sq. cm. (shearing stress P), is proportional to the velocity differential dv/dn between these two layers (where v is the velocity, and dv/dn is at right angles to the direction of flow) and to the constant η, which is the viscosity of the particular liquid:

$$P = \eta.dv/dn \tag{1}$$

This Newton law of friction fixes the magnitude of the viscosity η; in the c. g. s. system the shearing stress is in dynes per sq. cm., the velocity differential dv/dn is based on 1 second, and therefore η is in dynes per second per sq. cm. or poises (P).

To obtain an idea of this unit of viscosity, it may be noted that water at $20.2°$ C. has a viscosity of $0.01\ P$ or $1\ cP$ (centipoise).

In Newtonian liquids the viscosity η does not depend on the absolute magnitude of P or of dv/dn, but only on their ratio, so that it is immaterial under what experimental conditions η is determined, as long as laminar flow is taking place. Otherwise the conditions are those of non-Newtonian liquids, to which rubber solutions belong. With these liquids flow takes place under the slightest external force, but the viscosity does not depend on the values of P and dv/dn, for these liquids do not conform to the Newtonian friction law. It is for this reason that they have been characterized as non-Newtonian.

This dependence on experimental conditions can be expressed in any way which seems desirable. Theoretically the most satisfactory method is to follow that ordinarily used in mechanics to represent mechanical properties, viz., to express the properties in terms of the elemental volume. In this way the method is wholly independent of the particular apparatus employed. The experimental results obtained under a given set of conditions can then be applied, with the aid of certain hydrodynamic assumptions, to any other apparatus, i. e., the properties of the elemental volume are constant for the material.

On a basis of the Newtonian law, viscosity also is defined as a property of the elemental volume. Since at the present time insufficient data are at hand to formulate, in place of the Newtonian law, a new law on a sound theoretical and experimental basis, it will be shown in the following discussion how the problem can be approached indirectly, i. e., by the use of experimental data to formulate a friction law which is applicable to the liquid under investigation, and which is valid for this liquid under all conditions.

This can be effected by introducing the unknown function $f\ (P)$ in place of the Newtonian law. According to the procedure folowed by Porter and Rao,[29] Farrow, Neale, and Lowe,[30] Reiner,[25] and Weissenberg[26] there is obtained in this way the general non-linear law of friction:

$$dv/dn = f(P) \tag{2}$$

The problem involved in this theory is to derive, on a fundamental basis from molecular concepts, this unknown function, which as will be shown later can be determined experimentally.

To derive the function in this way, a definite type of flow based on known hydrodynamic principles is chosen for calculation, viz., laminar flow through a capillary. A similar calculation can be made with other types of flow, e. g., in a Couette apparatus, which consists of stationary cylinder and a concentric rotating cylinder.

The velocity distribution over the cross-section of the capillary is first calculated, this is then integrated, and the volume per second through the capillary is thus obtained. This calculation is based on the assumption that laminar flow is taking place, evidence of which has been discussed in detail elsewhere.[31] The part

played by the constriction at the end of the capillary tube can be disregarded if a sufficiently long capillary tube, i. e., one with a high ratio of length to diameter, is used.

For the type of flow in question through an infinitely long cylinder, the shearing stress P can be calculated from the equilibrium between the axial force, arising from excess pressure action at the end of the capillary, and the shearing stress P action at the surface of the cylinder.

$$\pi r^2 p = 2\pi r L P$$
$$P = \frac{rp}{2L} \tag{3}$$

Here r is the capillary radius (in cm.), L is the length of capillary (in cm.), and p is the difference in pressure between the ends of the capillary, i. e., the driving pressure (in dynes per sq. cm.).

Integration of Equation 2 after introduction of Equation 3 (cf. Kroepelin[15]) gives the following relation:

$$V = \frac{4Q}{\pi r^3}$$
$$= \frac{4}{Pr^3} \int_0^r Pr^2 f(Pr) dPr \tag{4}$$

Here $P_r = \frac{rp}{2L}$ is the maximum shearing stress at the periphery of the capillary and Q is the rate of flow (cc. per sec.).

In these calculations there is no connection between P and dv/dn, but only a relation between P and the mean rate of flow v (per sec.), which can be calculated both from measurements of the capillary and from experimentally determined values. The two relations are identical only in the case of Newtonian liquids; in other cases V is not identical with dv/dn, but is represented thus:

$$dv/dn = \frac{3V}{4} + \frac{P}{4} \cdot \frac{dv}{dP} \tag{5}$$

However, as an approximate calculation has shown, differences between dv/dn and V are in general small. As is evident from Equation 4 there is a functional relation between V and P_r without any other factors being involved. In both these expressions the constants, r, L, and P, of the apparatus are involved. Consequently if a solution is measured at a definite shearing stress P, the analysis of P into p, R and L is of no concern as long as laminar flow takes place. By means of this calculation, the extent to which the results are independent of the apparatus can be learned.

The functional relation between V and P may be designated as the flow curve. As will be shown later, these factors are related by a double logarithmic function (i. e., with the abscissa and ordinate as the logarithms of log V and log P, respectively, on suitable coördinate paper).

Let the quotient of P and V represent the apparent viscosity η':

$$\eta' = \frac{P}{V} \tag{6}$$

Then $\eta = \eta' = $ a constant for Newtonian liquids, whereas with non-Newtonian liquids η' can vary between a maximum value η_0 and a minimum value η_∞.

For Newtonian liquids, Equation 6 with introduction of the apparatus constants

assumes the form of the well known Hagen-Poiseuille law, where M is the volume of liquid (in cc.) which flows through the capillary in t seconds.

The derivations above therefore separate the Hagen-Poiseuille law into P and V. Based on analogy with Ohm's law of electricity, this new viscosity law defines the apparent viscosity η' as a resistance.

From the foregoing considerations, the flow curve, which may be regarded as an invariable characteristic of a solution, can be expressed in the following ways independently of the apparatus.

(1) Representation of V as a function of P on a logarithmic basis, according to Reiner[25] and Weissenberg.[26]

(2) Substitution of the absolute values of P and V by proportional values on a linear basis, viz., the volume of flow Q (in cc. per sec.) and the excess pressure P (in cm. of water), according to Herschel and Bulkley.[12]

(3) Substitution of V and P by the ratio of the viscosity of the solution to that of the solvent, i. e., the relative viscosity η_{rel}, which is then expressed as a function of the pressure P (in cm. of water or cm. of mercury). This is the most widely used method of representation (cf. Dogadkin and Pewsner[19]).

(4) Substitution of V by the value $Gf = 2/3\ V$, and representation of the relative viscosity η_{rel} or $\eta_{sp} = \eta_{rel} - 1$ (specific viscosity) as a function of Gf (cf. Kroepelin[15] and Staudinger[17]).

All these methods give identical results for a particular solution. When, however, the solvent or the temperature is changed, a thorough investigation of the most suitable manner of representation must be made. As long as one is not yet in a position to state whether structure viscosity is dependent on the shearing stress P or on the velocity of flow V, no final decision can be made. In view of this, in the following pages the theoretically more firmly established manner of representation as a flow curve on a logarithmic basis and over a small range of measurements, $\eta_{rel} = f(P)$, will be employed.

Apparatus

Having discussed the possibility of representing the properties of rubber solutions by flow curves, it seems fitting to describe the various types of apparatus which are adapted to the determination of these flow curves.

The most widely used types of apparatus are capillary viscometers. Of these the Ubbelohde viscometer[32] has an unusually great popularity, especially with the use of excess pressure, in which case the liquid is forced from one bulb into the other by means of compressed air, and the time required for this passage is determined (see Fig. 1). Other viscometers, which, however, have not been used to any considerable extent up to the present time for studying rubber solutions, include the overflow

Figure 1—The Ubbelohde Viscometer

viscometer of Wo. Ostwald and Auerbach[33] and the Tsuda viscometer,[34] the principles of which are evident in Figs. 2 and 3, respectively. The Bingham viscom-

eter as used by Herschel and Bulkley[35] conforms in principle to the Ubbelohde vis-
cometer, so that it seems unnecessary to describe it.

For the study of structurally viscous solutions, the present author has employed

Figure 2—The
Overflow Viscom-
eter of Wo.
Ostwald and
Auerbach

Figure 3—The Tsuda
Viscometer
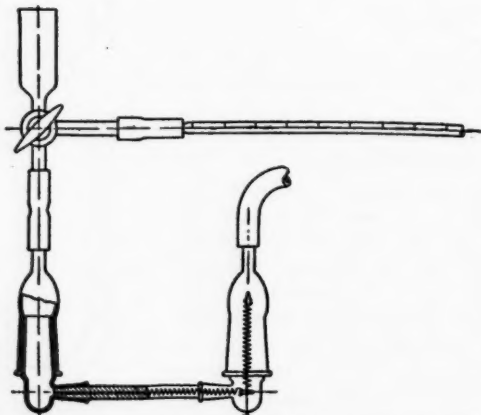
Figure 4—Glass Viscometer with Graduated Pipette

new forms of capillary viscometers,[36] which operate with excess pressure, and with
which the quantity of liquid flowing through the system is determined from the dis-

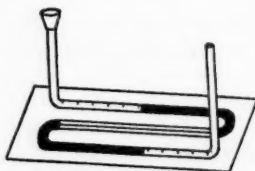placement of a drop of liquid in a graduated pipette.   The precision capillary tubes are accurately standardized and are exchangeable, so that by means of a wide range

Figure 5—High Pressure Viscometer with Gradu-
ated Pipette

of pressures a correspondingly wide range of shearing stresses and rates of flow can be measured within a convenient time interval.

The glass viscometer shown in Fig. 4 can be used with pressures up to 1 atmos-

Figure 6—Measurement of the Structural Viscosity According to
Kirchhof

phere; the high pressure apparatus shown in Fig. 5 up to 100 atmospheres. The same capillary tubes are used in the two viscometers.

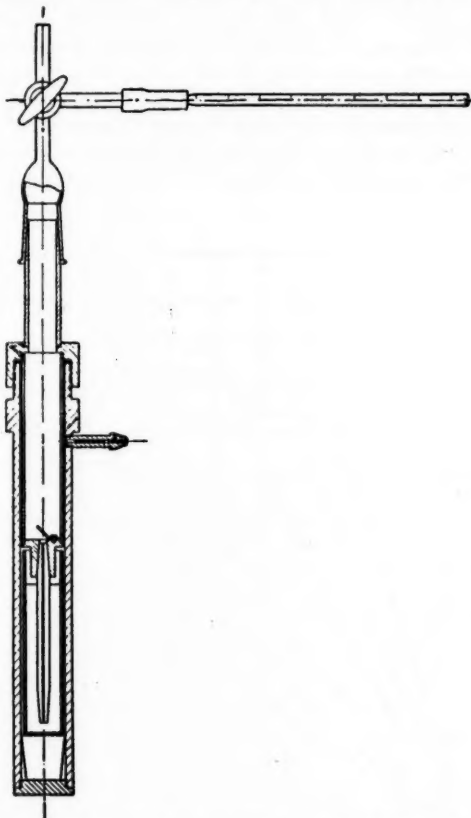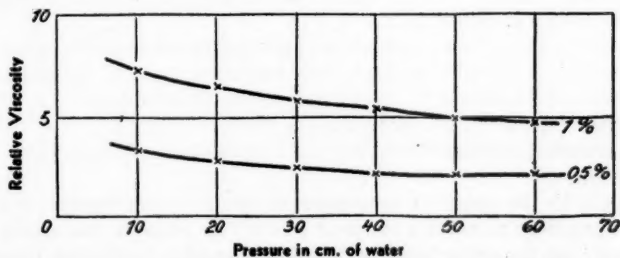Besides these, the falling-ball viscometers of Barthelmy,[37] Abernethy,[38] and Hirata and Kubo[39] are employed. With this type of viscometer, structure viscosity can be readily studied by means of different balls, but the range over which shearing stresses can be measured is necessarily small. Moreover it has not been possible up to the present time to establish shearing stress on a mathematical basis. For this same reason, the recently described Hoppler viscometer[40] is unsuitable for measuring the viscosity of rubber solutions. In the case of concentrated solutions of dead-milled rubber, as studied by Abernethy,[38] the falling-ball viscometer cannot
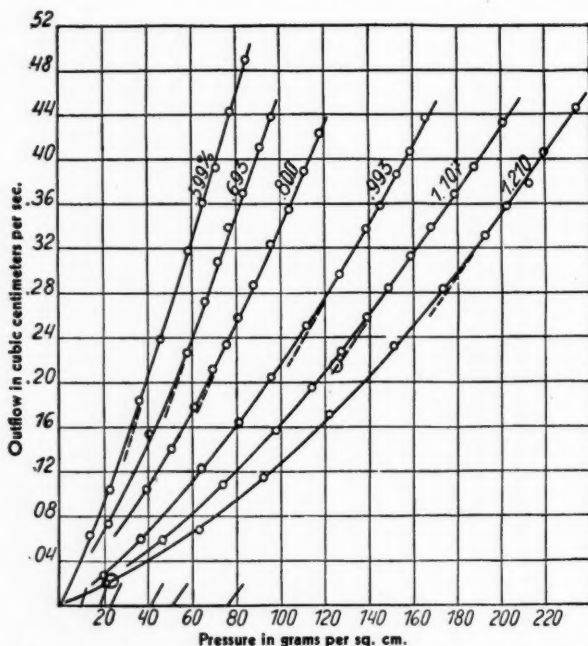
Figure 7—Measurements of the Velocity of Flow of Rubber Solutions by Herschel and Bulkley

be used, because these solutions have no demonstrable structure viscosity under the shearing-stresses in question.

The well-known Couette viscometer as employed by Hatschek[41] has been utilized only in a few instances for studying rubber solutions, e. g., by Hatschek[41] and by Reiner and Schoenfeld-Reiner.[42] As will be seen in the later discussion, the Couette apparatus gives results which agree from a practical point of view with those of capillary viscometers, so that it is a less questionable type of apparatus for measuring rubber solutions.

With respect to the range of measurement which is practicable, it is possible with a single capillary to cover a range of 1 to 100 in pressure and about 1 to 1000 in rate of flow; on the other hand, with interchangeable capillaries ranges of 1 to 10,000 in pressure and 1 to 10,000,000 in rate of flow are attainable.

85
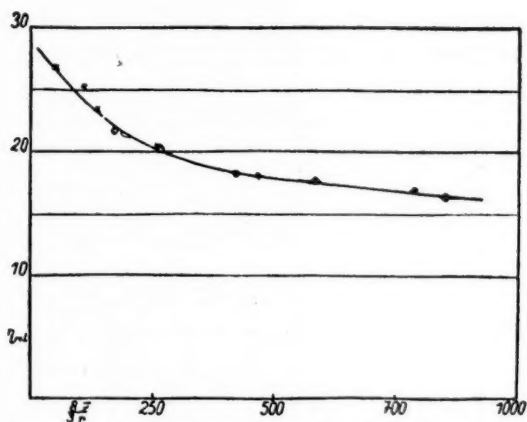
Figure 8—Measurements of Crepe Rubber in Benzene by
Kroepelin

   O   Measurements in Capillary III
   X   Measurements in Capillary V
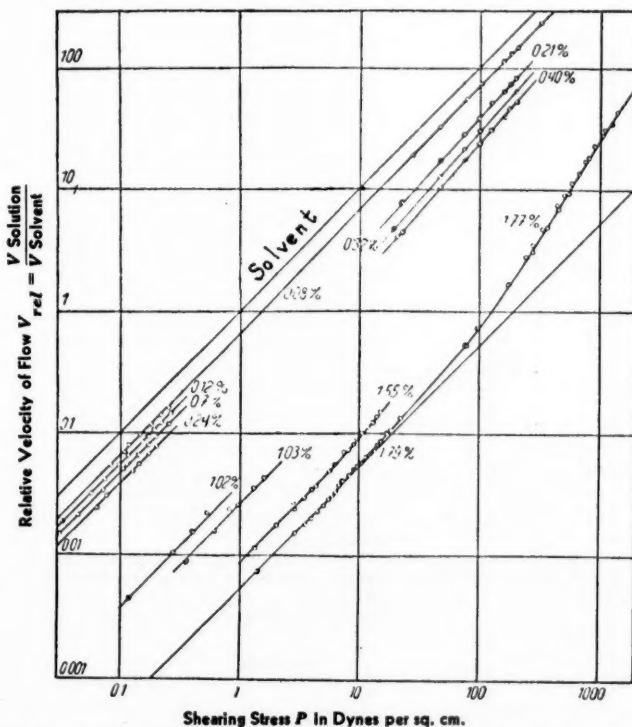
Figure 9—Flow Curves at Various Concentrations with Capillaries
and with a Couette Apparatus by Reiner and Schoenfeld-Reiner

Determinations of the Flow Curves of Rubber Solutions

As already mentioned, the first measurements of the structure viscosity of
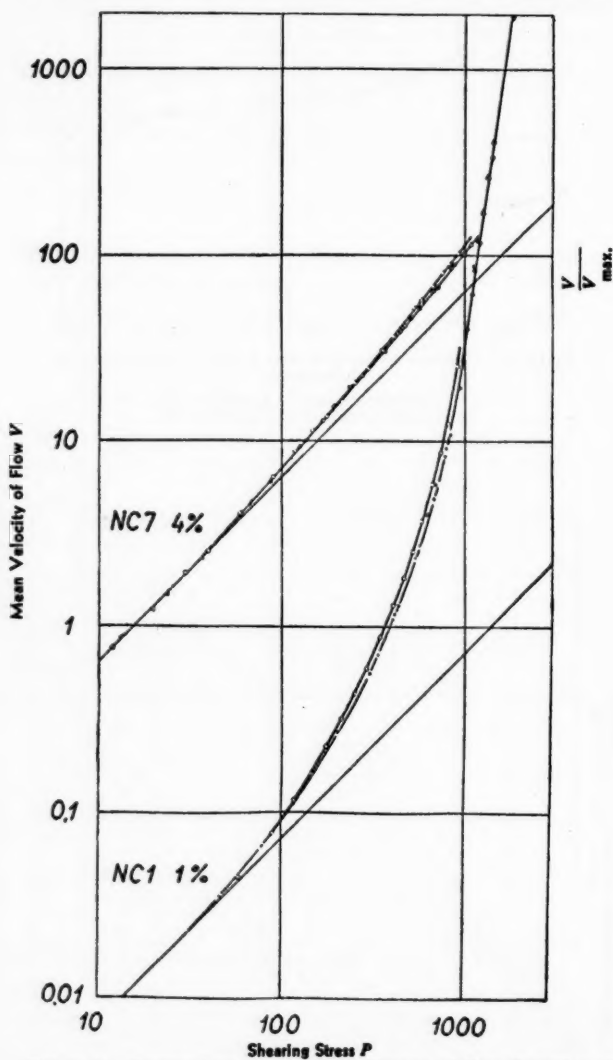
Figure 10—Comparison of the Flow Curves of Two Samples of Nitrocellulose and Butyl Acetate, Measured with a Capillary Viscometer and a Couette Apparatus

O	Couette Apparatus	
×	3.0	
+	2.0	
△	1.0	} Capillary
□	0.5	
▽	0.3	

rubber solutions were made by Fol[43] and Kirchhof.[44] Typical measurements of this property are shown in Fig. 6. Later Herschel and Bulkley[35] studied the structure

viscosity of benzene solutions; their results are shown in Fig. 7. This diagram shows in a particularly clear way that, with the linear scale used, the flow curves form an angle at the origin. This is evidence of a lack of any resistance to flow by these solutions. Furthermore it indicates that these solutions have a constant viscosity near the zero point. This will be more evident from other measurements
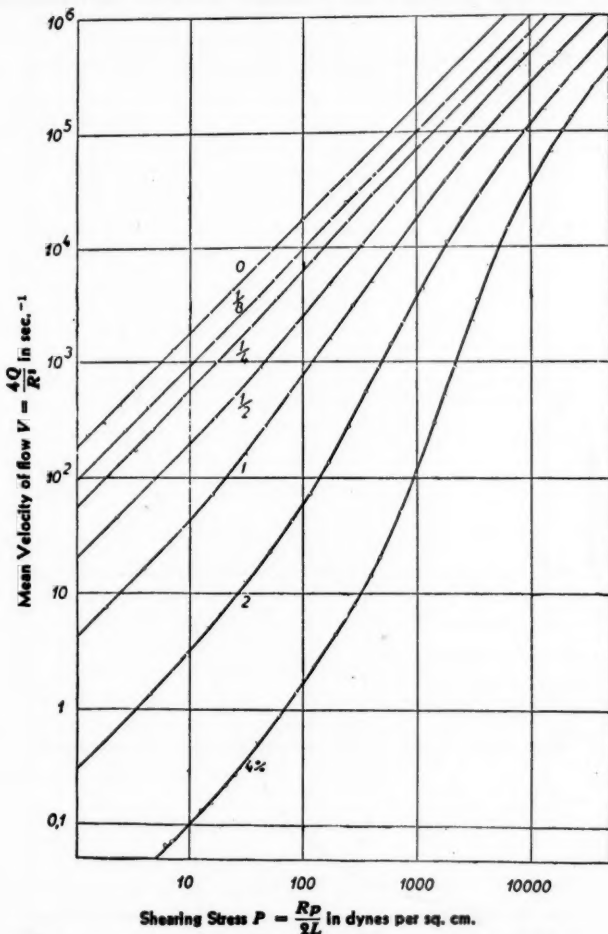
Figure 11—Flow Curves of Sheet Rubber over a Wide Range of Concentrations in Toluene

which will be described later. However, these measurements cannot yet be expressed in a form which is independent of the apparatus.

Measurements of the structure viscosity of rubber solutions have also been made by Wo. Ostwald[45] and by Ostwald and Föhre.[46] The first measurements and theoretical conclusions derived from them are those of Kroepelin[47] (see Fig. 8). As already mentioned, Kroepelin preferred to represent relative viscosity as a function of the velocity of fall, thus: $Gf = 2V/3$, a relation which was later utilized by Staudinger.

More recently Reiner[48] and Reiner and Schoenfeld-Reiner[42] have divided P into
r, L, and p in a systematic way, and have demonstrated that the flow curve of a
capillary viscometer is independent of the dimensions of the capillary, as is to be
expected on theoretical grounds.   They also showed, by means of comparative
measurements with capillaries and with a Couette apparatus, that these results do
not depend on the type of apparatus.   Naturally, however, the measurements with
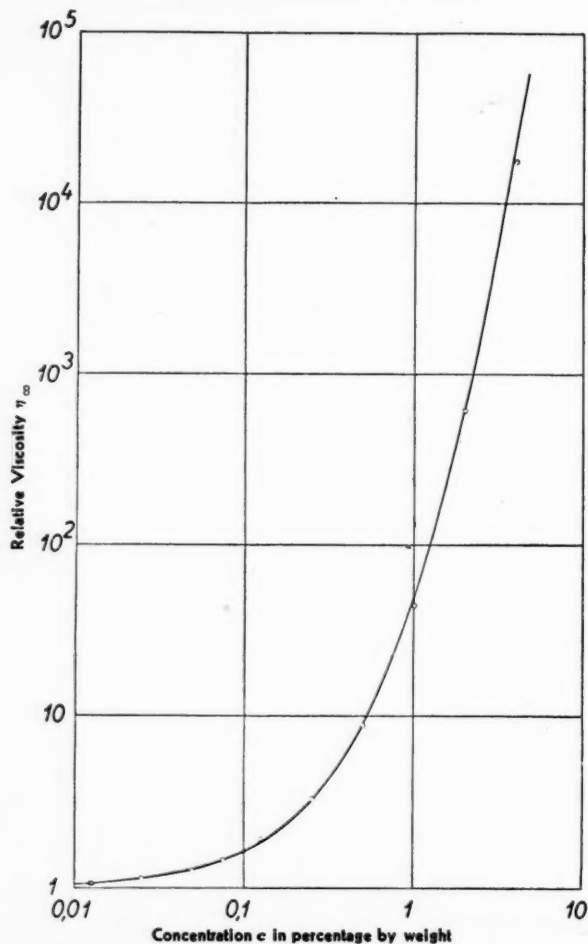
Figure 12—η_∞ as a Function of the Concentration, Derived from
the Data of Figure 11

the Couette apparatus were carried out at shearing stresses different from those
with capillary tubes, so that final conclusions cannot be drawn from the work.
These measurements of Reiner and of Reiner and Schoenfeld-Reiner are shown in
Fig. 9, and they give a good idea of the dependence of the flow curve on the con-
centration.

The present author[49] has attacked anew this problem experimentally, and has

shown that with nitrocellulose solutions, the behavior of which in this respect resembles closely that of rubber solutions, changes from one capillary to another can be made over a very wide range, and measurements with a Couette apparatus differ to only an insignificant extent theoretically (approximately 10 per cent) from those with a capillary viscometer. In comparison with the large effect of shearing stress, these differences are unimportant, so that the troublesome technique of the Couette apparatus can be avoided. A comparison of the Couette apparatus and capillary viscometer is shown in Fig. 10.

In further work with the viscometers mentioned, the present author has studied the flow curve as a function of concentration over the wide range of shearing stresses possible with the Couette apparatus. The results are shown in Fig. 11. This logarithmic representation of the experimental results makes plain the S-form of the flow curve, i. e., the change in the apparent viscosity between the limits of an η_0 and η_∞.

If the lower parts of the curves are transcribed to a linear scale, the results correspond to those of Herschel and Bulkley. As is evident from all the experimental results described, the curves in Fig. 11, because of the wide range which they cover, give a comprehensive picture of the dependence of the flow curve on concentration.

This behavior of rubber solutions is not unique, but is also manifest with other lyophilic colloids, especially cellulose derivatives and starch.

The S-form of the flow curve makes it possible, as mentioned in the beginning, to derive the constants η_0 and η_∞, the dependence of which on various influences can then be studied.

At the same time an elasticity modulus γ enters into play in the case of rubber solutions, and this is of great importance. Since, however, entirely different methods of measurement are necessary to determine its magnitude, it will be dealt with in a special work.
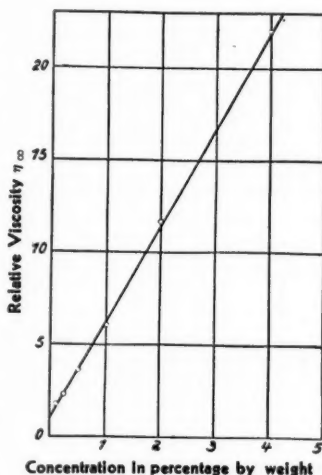
Figure 13—η_∞ as a Function of the Concentration, Derived from the Data of Figure 11

The Dependence of Viscosity on Concentration

From Fig. 11 the dependence of the viscosities η_0 and η_∞ on the concentration can be obtained directly. This relation is shown in Figs. 12 and 13. It should be noted that in most of the measurements η_∞ was not determined, and that the value ordinarily designated as the "viscosity of rubber solutions," which under certain conditions is diminished by the structure viscosity, corresponds to the η_0 value.

The well-known way in which viscosity varies so greatly with concentration is evident in Fig. 12.

A survey of the large amount of data on the dependence of the viscosity of rubber solutions on the concentration, e. g., the results of Fikentscher and Mark,[50] Staudinger,[51] Kirchhof,[46] etc., shows that the dependence of η_0 on the concentration, as expressed by the logarithmic relation shown, remains independent of the viscosity of the particular solution itself. Even in the measurements of Abernethy at

concentrations up to 40 per cent, this relation holds true, as is seen in Fig. 14. It is, however, demonstrable only if the concentration c is expressed in per cent by weight, $i.\ e.$, grams of rubber per 100 grams of solution.

The invariable form of the η_0-c curve indicates that the dependence of η_0 on the concentration depends in turn only on one constant, which may be designated $[\eta]$. This $[\eta]$ constant corresponds to the slope of the η_0-c curve at the zero point on the linear scale, or to the η_{sp}/c value of Staudinger.[51] Consequently the viscosity of a rubber solution depends on this constant $[\eta]$ and on the concentration.
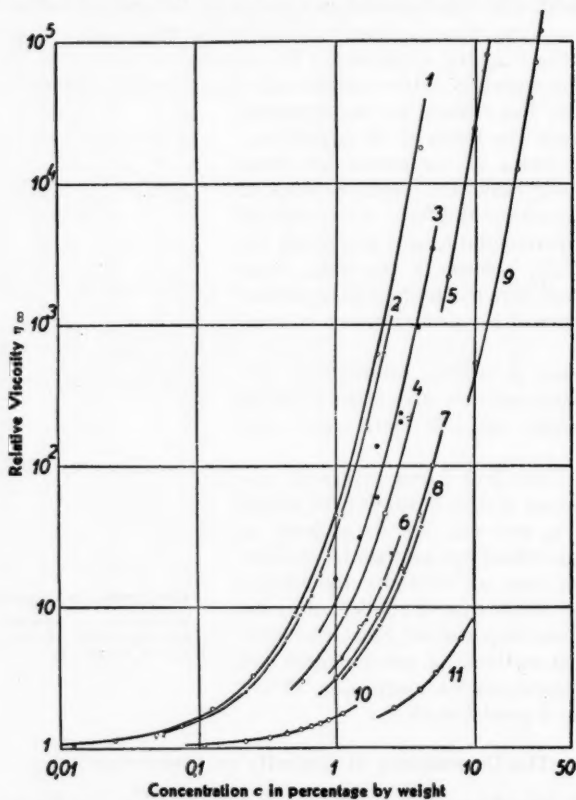
Figure 14—η_∞ as a Function of the Concentration of Various Types of Rubber, as Derived from the Data in Table I

Under conditions where η_0 is obtained by a proper choice of shearing stress, the $[\eta]$ value can be calculated from a single viscosity determination. In view of the fact that the concentration function is valid over a wide range (1 to 10,000), the changes which have been proved to be true of dilute solutions are especially true of very concentrated solutions. The course of the curve in Fig. 13 can, like most empirical relations, be expressed by a series of mathematical relations. The formulas of Fikentscher,[52] Kruyt, Bungenberg, de Jong, and Lens,[53] and of Baker[54] have proved of especially great value. That of Fikentscher is:

$$\log \eta_{rel} = \frac{c(k + 75kc)}{1 + 1.5kc} \tag{8}$$

where c is the volume percentage of c grams of substance per 100 cc. of solution, and k is the specific viscosity of Fikentscher.

The formula of Kruyt, Bungenberg, de Jong, and Lens has recently been employed by Staudinger and Heuer.[54] It is:

$$\log (\eta_{sp}/c) = \log [\eta] + k_{st}c \tag{9}$$

where k_{st} is the gradient constant.

The formula of Baker as changed by the present author in collaboration with Hess[55] is:

$$\eta_{rel} = \left(1 + \frac{c[\eta]}{8} \right)^{8} \tag{10}$$

With the aid of Equation 10, the data available in the literature have, in the present paper, been converted into $[\eta]$, i. e., to a basis independent of the concentration. This way of expressing data has direct advantages, especially the possibility of comparing various influences on the same basis.

It must, however, be realized that, because of the extraordinary sensitivity of the viscosity of rubber solutions to the influence of light and atmospheric oxygen, reliable measurements at a series of concentrations involve certain difficulties.

Very recently Mojen[56] has studied the influence of concentration on a series of masticated rubbers and hydrorubbers. The much more stable hydrorubbers conform more closely to Equation 10 than do corresponding solutions of crude rubber. Moreover, Equation 10 is valid only for η_0, so that only by taking into account the structure viscosity by measurements at various shearing stresses can these simple relations be derived.

TABLE I
DEPENDENCE OF η_0 ON THE CONCENTRATION FOR VARIOUS RUBBERS CONVERTED TO $[\eta]$ VALUES

Curve	Material	Solvent	$[\eta]$	Observer
1	Sheet Rubber	Toluene	4.85	Philippoff
2	Crepe Rubber	Chlorobenzene	4.20	Fikentscher[50,52]
3	Smoked Sheet	Xylene	3.40	Bary and Fleurent[58]
4	Sheet Rubber	Pentachloroethane	2.13	Kirchhof[44]
5	Masticated Crepe	Toluene	2.00	Philippoff
6	Bromorubber	Chlorobenzene	1.45	Fikentscher[52]
7	Degraded Rubber	Xylene	1.21	Bary and Fleurent[58]
8	Hydrorubber (25,000)	Tetralin	1.11	Mojen
9	Dead-milled Rubber	Toluene	0.89	Abernethy[35]
10	Dead-milled Rubber	Chlorobenzene	0.53	Fikentscher[50]
11	Hydrorubber (5000)	Tetralin	0.40	Mojen[56]

It should be emphasized that, as has been proved for cellite solutions,[57] a series of solutions of various concentrations must be prepared from a stock solution of the maximum concentration and not by a series of weighings. This is of particularly great importance in the case of crude rubber, which contains impurities, such as resins and protein, probably dispersed irregularly throughout the mass of rubber.

To show by an example to what extent Equation 10 holds true, the values in Fig. 12 are reproduced in Table II, together with the $[\eta]$ values.

The maximum deviation of the $[\eta]$ constants calculated from each concentration is only 4 per cent of the mean value, which seems unimportant from a practical point of view.

The relations are complicated by the fact that viscosity depends to such a great extent on concentration, i. e., effects which in dilute solutions are within the

TABLE II

DEPENDENCE OF η_0 ON THE CONCENTRATION FOR CRUDE SHEET RUBBER
(Measurements in Toluene Solutions at 20° C.)

Concentration (Percentage by weight)	η_{rel}	$[\eta]$
4	17,500	4.78
2	620	4.92
1	44	4.84
0.50	9	5.04
0.25	3.3	5.11
0.125	1.9	5.25
0.075	1.44	5.01
0.050	1.264	4.75
0.025	1.135	5.12
0.0125	1.063	4.86
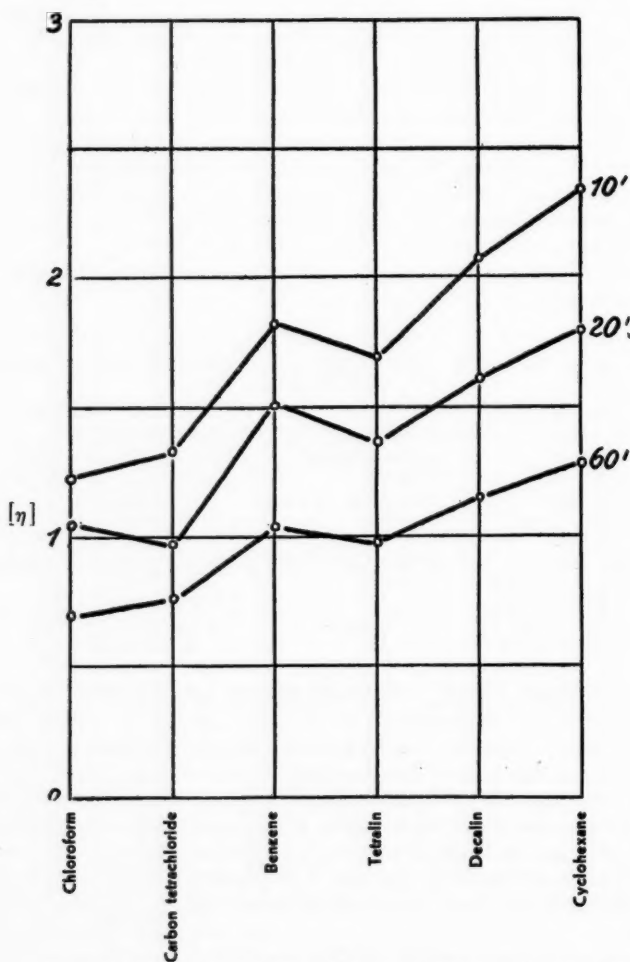
Figure 15—Dependence of $[\eta]$ of Masticated Rubber on the Solvent, according to Mojen

experimental errors can play a decisive role in concentrated solutions. This is particularly true of the effects of the solvent and the temperature. By utilizing the factor $[\eta]$, which is independent of concentration, these complicating effects are avoided.

The *viscosity number VN*, introduced by Fol[12] represents the surface area which is bounded by the concentration-viscosity curve, the specific viscosity at 1 per
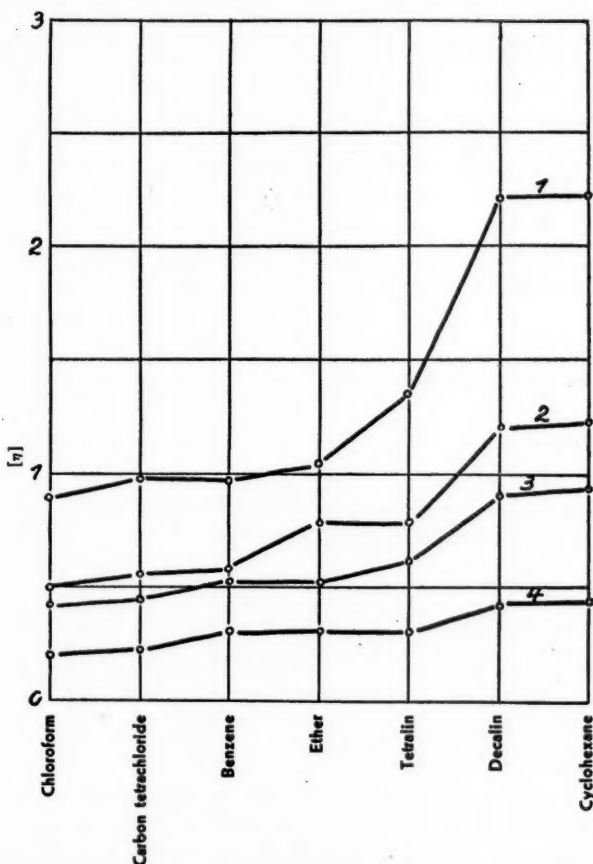
Figure 16—Dependence of $[\eta]$ of Hydrorubber on the Solvent, according to Mojen

cent concentration and the abscissa axis, and is related to the constants of Equation 10 as follows:

$$VN = \int_0^1 \left(1 + \frac{c[\eta]}{8}\right)^8 dc - 1 = \frac{8}{9}[\eta]\left\{\left(1 + \frac{[\eta]}{8}\right)^9 - 1\right\} - 1 \quad (11)$$

From this equation it is easy to construct a curve from which VN can be converted into $[\eta]$ and *vice versa*. As is known, the viscosity number VN has been employed at the Netherlands Government Rubber Institute.

The Dependence of Viscosity on the Solvent

Since the investigations of Kirchhof published in 1914,[44] it has been known that not only the absolute viscosity of rubber solutions (in poises) but also the relative viscosity η_{rel} (which is relatively independent of solvents) vary with the solvent. Recently this problem has been investigated by Kawamura and Tanaka,[59] Sakurada and Tanaka,[60] and Mojen,[56] and only as a result of their work have any quantitative data been made available.

A summary of the results of the Japanese investigators is shown in Tables III and IV, while the experiments of Mojen, which were carried out with two series of masticated rubber and hydrorubber samples, are shown in Figs. 15 and 16. It may be seen from these data that, as far as the subject has so far been pursued, the $[\eta]$ values of both rubber and nitrocellulose[57] depend, within the range of about 1 to 2, on the solvent, almost irrespective of the viscosity of the preparation. Therefore this factor has a multiple influence on the viscosity. As will be explained later it is related in many ways to the solvation of the rubber particles.

TABLE III

INFLUENCE OF THE SOLVENT ON THE $[\eta]$ VALUE OF SMOKED SHEET

Data of Kawamura and Tanaka, in 0.25 Per Cent by Volume at 25° C.

Solvent	η_{rel}	Density of Solvent	$[\eta]$
Carbon Tetrachloride	6.01	1.594	5.04
Petroleum Benzine Alcohol	2.60	0.88	5.99
Xylene	4.97	0.86	8.23
Chloroform	4.00	1.48	4.10
Benzene Alcohol	2.73	0.88	4.89

TABLE IV

INFLUENCE OF THE SOLVENT ON THE $[\eta]$ VALUE OF PURIFIED RUBBER

Data of Sakurada and Tanaka; $[\eta]'$ Based on Percentage by Volume of Solvent

Solvent	$[\eta]'$	Density of Solvent	$[\eta]$
Petroleum Ether	5.05	0.88	5.74
Carbon Disulfide	6.33	1.26	5.00
Benzene	6.85	0.88	7.80
Carbon Tetrachloride	7.94	1.59	4.97
Chloroform	5.82	1.48	3.92
Tetralin	5.92	0.97	6.04
Trichloroethylene	5.95	1.47	4.05
Chlorobenzene	6.21	1.11	5.61

The solvent which gives the lowest viscosity of a rubber solution is carbon tetrachloride (with chloroform and trichloroethylene, the influence on the viscosity of the hydrochloric acid formed on standing is uncertain); the solvents which give the highest viscosities are cyclohexane and xylene. Between these lie benzene and toluene, which are probably the most widely used solvents for viscosity measurements.

Any conclusions regarding the effect of the affinity of the solvent on the viscosity would be premature in view of the unsatisfactory experimental data, which are small in amount and at the same time contradictory. For example, according to Mojen, carbon tetrachloride and benzene have about the same effect, whereas according to Sakurada and Tanaka benzene gives solutions with almost 60 per cent higher viscosities than does carbon tetrachloride,

Effects similar to those of individual solvents are shown by mixtures of solvents, and by mixtures of solvents and precipitating agents, as has been shown, for ex-

ample, by Kawamura and Tanaka. Because of the peculiarities of the temperature coefficient, these experiments are discussed in the following section.

The Dependence of Viscosity on Temperature

The dependence of the viscosity of rubber solutions on their temperature has been investigated repeatedly. As already mentioned, Abernethy[38] published the first fairly precise measurements of concentrated solutions of dead-milled rubber
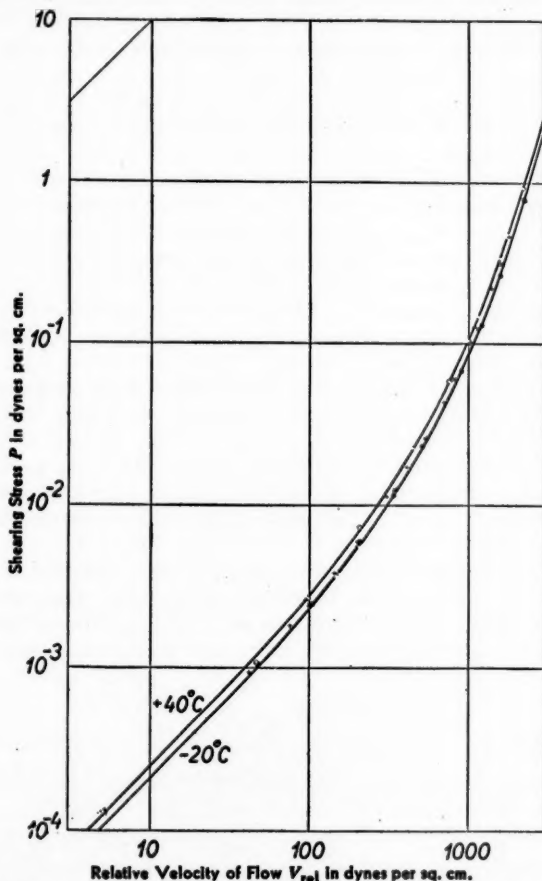
Figure 17—Flow Curves of a 4 Per Cent Solution of Sheet Rubber in Toluene as a Function of the Temperature between −20° C and 40° C.

in toluene. He found a slightly negative temperature coefficient (TC), $i.\ e.$, a diminution in viscosity with increase in temperature. This was confirmed by Busse and Karrer,[61] by Dogadkin and Lawrenenko,[62] and by others.

On the contrary, Haller[63] found a positive temperature coefficient, $i.\ e.$, an increase in the relative viscosity with increase in temperature. Then again Reiner and Schoenfeld-Reiner[42] found a zero temperature coefficient of the flow curve.

To throw further light on this problem, the present author carried out a series

of experiments with a 4 per cent solution of smoked sheet in toluene between $-20°$ C. and $40°$ C. The results are shown in Fig. 17. To compare these experiments with one another at different temperatures, the "relative velocity of flow" is shown instead of the mean velocity of flow V proposed by Reiner and Schoenfeld-Reiner.[42] This relative velocity of flow is the ratio of the velocity of flow of the solution to that of the solvent at a shearing stress P of 1 dyne per sq. cm.

In spite of the extremely great range of measurement, *viz.*, 1 to 10,000, and a relative viscosity over 10,000, a change of only 17 per cent was found for a temperature change of about $60°$ C. This may be regarded as negligibly small. Accordingly these measurements can be regarded as a confirmation of the results of Reiner.

However, as has already been pointed out by Dogadkin and Lawrenenko,[62] it is not justifiable at this time to extend these conclusions to other types of rubber or to other concentrations.

To what extent the relations are complicated is shown by the experiments of Kawamura and Tanaka (Table V), who found that by addition of a precipitating agent (methanol) to solutions of rubber in benzene at $25°$ C. and $50°$ C. there was a reversal of the temperature coefficient with increase in the proportion of methanol. This means that both the magnitude and the mathematical sign of the temperature coefficient are greatly influenced by the solvent. In general, however, these changes in temperature coefficient are much smaller than in the case of solutions of cellulose derivatives.

A more exhaustive investigation of the dependence of the temperature coefficient on the solvent would doubtless solve this problem. It is nevertheless improbable, in view of the certain validity of Equation 10, that, as indicated by Dogadkin and Lawrenenko, the temperature coefficient changes with change in concentration. If the temperature coefficient is referred to $[\eta]$ rather than to the relative viscosity at the particular concentration, the result is, as might be anticipated, independent of the concentration.

Considered in this way, the term temperature coefficient obviously refers only to a reversible temperature coefficient, which leaves the viscosity unaltered at $20°$ or $25°$ C. when the solution is heated or cooled. The irreversible influence of temperature on viscosity, *i. e.*, the thermal degradation, is discussed independently later.

<div align="center">TABLE V</div>

<div align="center">INFLUENCE OF THE PRECIPITATING AGENT ON THE VISCOSITY $[\eta]$</div>

Data of Kawamura and Tanaka. 0.25 Per Cent by Volume of Smoked Sheet in Benzene + Methanol at Two Different Temperatures

Percentage of Methanol		0	2.5	5	10	15
η_{rel}	at $25°$ C.	4.12	2.89	2.72	2.46	1.89
	at $40°$ C.	3.73	2.81	2.69	2.53	2.07
$[\eta]$	at $25°$ C.	5.34	3.90	3.68	3.27	2.28
	at $40°$ C.	4.92	3.80	3.62	3.38	2.61

Characterization of Rubber by Viscosity Measurements

The various factors just discussed which influence viscosity, *viz.*, shearing stress, concentration, solvent, and temperature, result in widely varying viscosities of solutions of the same sample of rubber.

With the aid of a flow curve and the η_0 value derived from it, the results are independent of the shearing stress and therefore of the apparatus. Furthermore with $[\eta]$, one is independent of the concentration. Up to the present time, however,

it has not been possible to obtain similar data on the influence of the solvent and temperature, and one must be content with a reference solvent, *e. g.*, toluene, xylene, or carbon tetrachloride at 20° C. or 25° C.

It is then possible to formulate a series of experimental conditions governing the way in which viscosity measurements are to be made in order to obtain a reliable value for $[\eta]$.

(1)   Preparation of a solution under reproducible conditions, including drying, agitation, etc.   Filtration under pressure (a few cubic centimeters of mercury) is strongly recommended.

(2)   Measurement of η_0, taking into account the structure viscosity with the aid of a portion of the flow curve.   An apparatus of the type described is suitable for this.

(3)   In the measurement of a series of concentrations, the preparation of a stock solution, which can then be diluted, is advantageous.

(4)   The data can be conveniently expressed as relative viscosities, *i. e.*, the ratio of viscosity of solution to viscosity of solvent, in which case the concentration c is expressed in percentage by weight.

(5)   In the determination of relative viscosities, care must be taken that unconditional laminar flow takes place during the measurements; otherwise uncontrollable disturbances will enter into play.   From a practical point of view, this exaction means a maximum rate of flow in the viscometer of approximately 0.05 cc. per second, *i. e.*, a time of flow of 40 to 50 seconds in ordinary viscometers of 10 cc. capacity.   This exaction is frequently ignored, *e. g.*, in studying concentrated solutions, times of flow of only 7 to 10 seconds for the solvent have been employed. In measurements of viscous solutions (around 1 poise and more) this difficulty can be avoided by the use of two different viscometers or interchangeable capillary tubes, as was done by Bary and Fleurent, Reiner, and the present author.   In this case η_{rel} is calculated from the absolute viscosity.

(6)   In viscosity data, temperature and solvent must be given under all conditions.   This is frequently neglected.   If the measurements are confined to one shearing stress, this particular shearing stress P must be given ($P = Rp/(2L)$, where R is the radius of the capillary tube, L is its length in centimeters, p is the excess pressure in dynes per sq. cm., or as usually expressed, p is the height h in centimeters of a liquid column of density ρ, or p in dynes per sq. cm. $= 981\ h\rho$).

With these data a determination of $[\eta]$ is possible.

One of the properties which is employed to a wide extent to characterize liquids is viscosity.   As is well known, this property also serves to compare samples of rubber, in which case the viscosities of the rubbers are measured in organic solvents.

However, the value which is usually regarded simply as the viscosity is, in contrast to the viscosity of low-molecular substances, a complex function of various influences which are usually ignored.   The chief peculiarities of the viscosity of rubber solutions, which are also characteristic of solutions of other organic and synthetic colloids, are a high viscosity, even of dilute solutions, and a structure viscosity, which is manifest in a diminution of the measured viscosity with increasing pressure and velocity of flow.   The structure viscosity can, under certain conditions, reduce greatly the validity of conclusions from viscosity measurements, and it has frequently been of aid to recognize the existence of this property, even when it has not been investigated further.

However, as extensive investigations at the Institute of the present author have shown, structure viscosity may be of aid in solving a long series of problems which have not been attacked heretofore, *e. g.*, the possibility of comparing the properties

of various types of rubber in a much more thorough manner, since more factors than just the viscosity can be studied by the methods applied.

For a comparison plastometer measurements can be utilized, but in the study of solutions rather than rubber in the solid state the range of measurement attainable is nevertheless considerably greater (several ten powers), and the apparatus is much less complicated and less sensitive mechanically than is the plastometer.
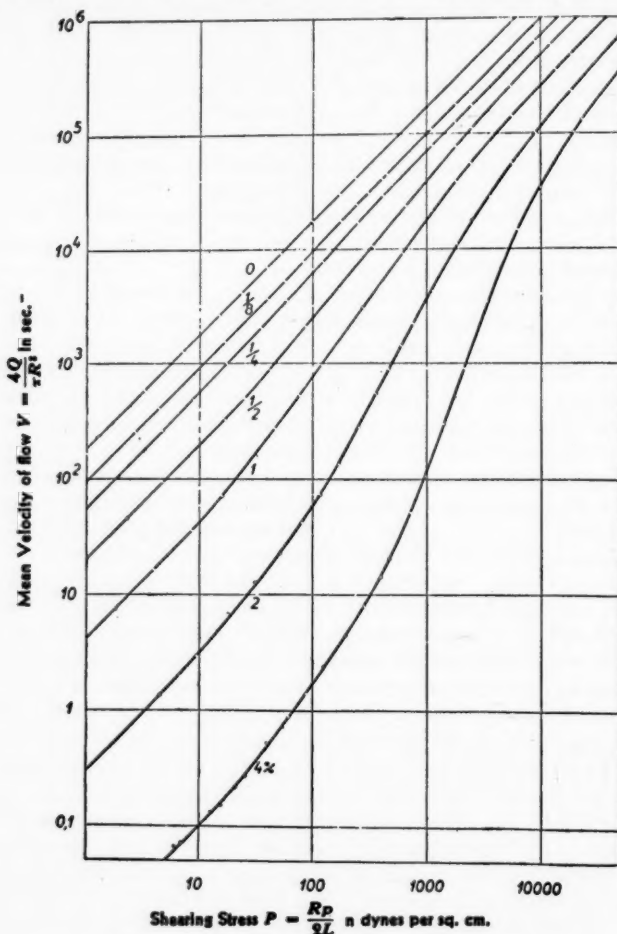
Figure 18—Flow Curves of Sheet Rubber in Toluene

Of course plastometer measurements are applicable to finished mixtures, whereas measurements of solutions can be made only on raw mixtures or on slightly vulcanized mixtures. Nevertheless it would appear to be advantageous to supplement plastometer measurements with the much more easily carried out viscosity measurements with a view to characterizing various types of rubber.

On account of the anomalies in viscosity which have been mentioned, it seems fitting to summarize the recent publications on the viscosity of rubber solutions with a view to obtaining a comprehensive idea of the subject.

First of all there is the problem as to how solutions with variable viscosities are to be described, and to what constants they may be referred. As has been shown, this is best done by means of a flow curve, which represents in logarithmic form the mean velocity of flow V as a function of the shearing stress S.

The ratio : S/V represents the apparent viscosity η', which is constant for normal liquids, but which varies from a maximum η_0 value to a minimum η_∞ value for structurally viscous liquids. On the logarithmic scale used, these two limits correspond to a trend of the flow curve below 45° C. Fig. 18 shows flow curves which were constructed from data on solutions of various concentrations of smoked sheet in toluene. It is evident from these curves that the expected S form is a characterisitic of all curves, and that a very broad range of measurements, such as is not ordinarily used in technical work, is necessary to make this shape evident.
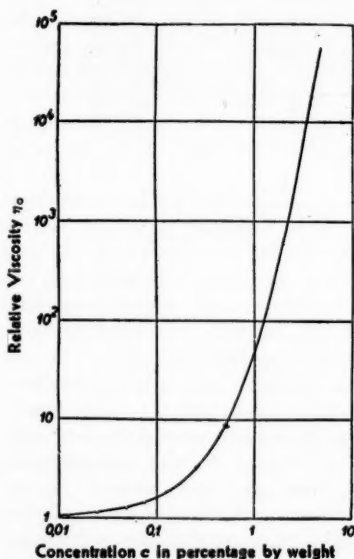
Figure 19—η_0 as a Function of the Concentration Derived from the Data of Figure 18
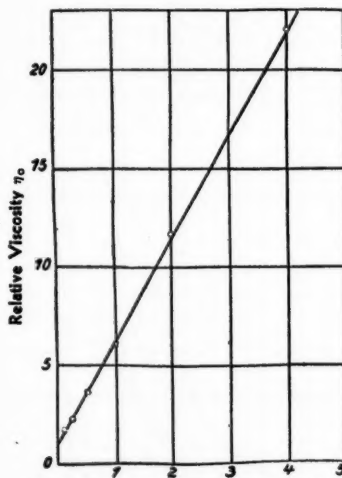
Figure 20—η_∞ as a Function of the Concentration, Derived from the Data of Figure 18

The flow curve is, over a wide range, independent of the apparatus, and it represents a material constant of a solution. Likewise its limits, η_0 and η_∞, are material constants of the particular solution. In order to be independent of concentration, empirical concentration functions have been derived, which for η_0 and η_∞ are as follows:

$$\eta_0 = \left[1 + \left(\frac{[\eta]}{8} \right) c \right]^8 \tag{12}$$

$$\eta_\infty = K_\infty c \tag{13}$$

where $[\eta]$ and K_∞ are characteristic constants and c is the concentration (in percentage by weight). The validity of Equation 12 and Equation 13 is evident from Figs. 19 and 20, in which the theoretical curves are drawn through the experimental points obtained from Fig. 18. It is seen that even in the case of

the most anomalous (with respect to viscosity) rubber solutions, mathematical formulas are applicable, a fact which is surprising in view of the otherwise badly defined mechanical properties.

Formula 12 is applicable to most types of rubber, as is particularly evident in Fig. 21, in which a series of viscosity measurements taken from the literature are shown.

The $[\eta]$ value is then of good service in characterizing various types of rubber, and it corresponds to the η_{sp}/C constant of Staudinger, which is a function of the molecular weight. The difference between these two constants lies in the fact that $[\eta]$ is based on percentage by weight and η_{sp}/C on base mols per liter. $[\eta]$ has an obvious meaning when it is expressed as a function of the concentration on a linear scale: for here it corresponds to the slope of the curve at the zero point.
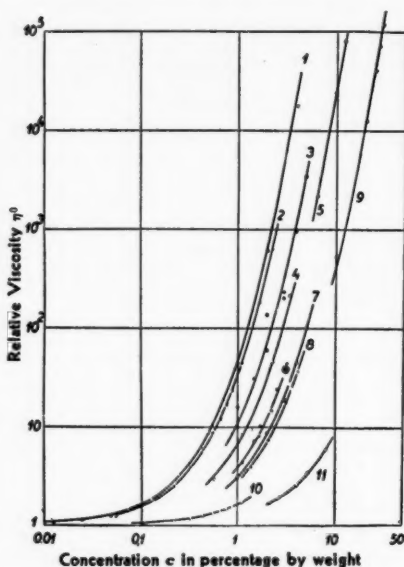
Figure 21—η_0 as a Function of the Concentration for Various Types of Rubber

It should be pointed out that, while the flow curve is drawn on an absolute scale, Formula 12 is based on relative viscosities, i. e., on the ratio of the viscosity of a solution to the viscosity of the solvent, while Formula 13 is based on specific viscosities, i. e., $\eta_{\text{sp}} = \eta_{\text{rel}} - 1$.

To use these formulas in experimental work, it is therefore necessary to know accurately the viscosity of the solvent, and in many cases, e. g., with very viscous solutions, it is advisable to determine the relative viscosity indirectly from the absolute viscosity.

For characterizing rubber samples as discussed earlier, the $[\eta]$ value first of all and then the course of the flow curve of a solution of definite concentration, e. g., one per cent, are of decisive importance. Studies of nitrocellulose, to which recourse must be had for lack of corresponding measurements of rubber solutions, have shown that η_∞ is practically independent of the properties of different samples, so that differences in samples are manifest primarily by the η_0 values and therefore by the $[\eta]$ values. Accordingly the course of the flow curves between these limits can have differing degrees of flatness, and such differences are of service in characterizing a rubber.

As was discussed in the foregoing summary, the $[\eta]$ value depends on a number of influences, such as heat, mastication, vulcanization, acceleration, solvent, and temperature. A survey of the results of studies of these various influences would lead too far afield.

As has been proved theoretically by Weissenberg, structure viscosity must bear some relation to a form-elasticity. A structurally viscous substance must correspond in a qualitative way to so-called Maxwell substances, which have certain properties different from those of normal liquids. Thus under constant stress a Maxwell substance flows steadily; at a fixed and constant deformation the stress diminishes exponentially with time; subjected to deforming oscillations, the damp-

ening effect, *i. e.*, the viscosity, and the elasticity depend on the frequency of oscillation.

All these phenomena are manifest in solutions of lyophilic colloids and also in rubber solutions, but the quantitative relations between the individual influences is complicated, as would be expected on a basis of the Maxwell phenomena.
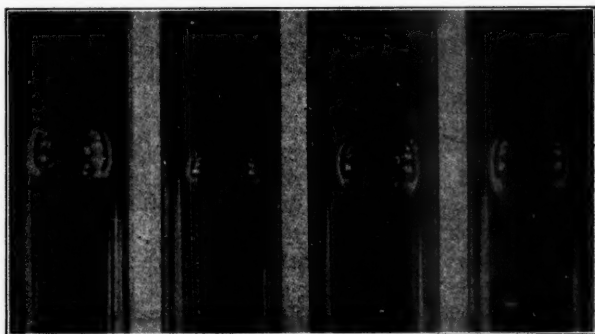
Figure 22—Ascending Air Bubbles in Colloidal Solutions
1. Ammonium Lactate Solution as a Control
2. Cellit in Dioxan, Time Constant about 0.01 Sec.
3. Nitrocellulose in Amyl Acetate, Time Constant about 0.5 Sec.
4. Nitrocellulose in Amyl Acetate, Time Constant about 1.5 Sec.

Since experiments which are adapted to studying the elasticity of colloidal solutions have not found general usage, it seems advisable to discuss them here.

The first case, steady flow, is self-explanatory. The second case, a decrease with time in tension and of the properties in general which are a function of time, can be readily demonstrated by a simple experiment.

If an air bubble is allowed to rise through a colloidal solution in a tube (see Fig. 22) it will be noticed that the bubble assumes the form of a drop, and flows with its lower part in pointed form. In normal liquids of the same viscosity (a concentrated solution of ammonium lactate was employed), the ends of the bubbles have a normal, almost spherical contour. The greater the "anomaly" of the colloidal solution, the greater is this characteristic deformation of the bubbles. This deformation is also related to those factors designated as "time constants."

The occurrence of this phenomenon can be explained on the assumption that the

Figure 23—Measurements of the Dampening Effect (Dynamic Viscosity η) of 6 Per Cent Toluene Solutions of Sheet Rubber (1) Crepe (2), and Para Rubber (3) as a Function of the Frequency

deformed liquid is pierced by the bubble, and this rupture can be repaired only after a certain length of time which depends on the time constants. This bubble phenomenon makes it possible to decide in a qualitative way whether a colloidal solu-

tion has elastic properties. The time constants of colloidal solutions can have widely varying values, *viz.*, from several seconds to several thousandths of a second.

The third type of elastic phenomena, *i. e.*, the dependence of viscosity and elasticity on frequency, has been studied at the Institute by the present author. The principle followed in the measurements was to determine the force on a rod which swings concentrically and axially in a tube filled with the experimental liquid. The force on the rod, and consequently the rate and frequency of the swings, can be altered and measured. Two methods are possible with which to measure on the one hand the dampening effect, and on the other hand the resistance to deformation, in other words, the total force of the liquid.

Results obtained in measurements of dampening are shown in Fig. 23, toluene solutions of like concentration of crepe, sheet, and Para rubber. Notwithstanding the approximately equal viscosities, the courses of the flow curves differ considerably. The curve for sheet rubber is "normal," and corresponds to results ob-
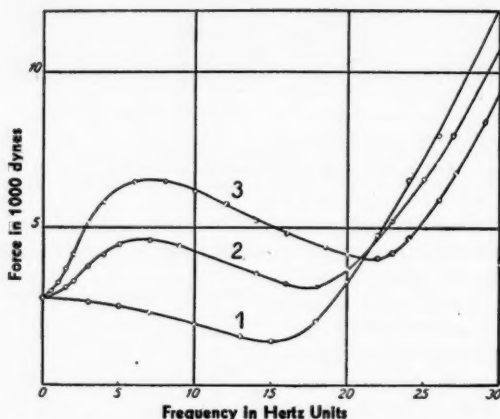
Figure 24—Total Force Exerted by the Liquid as a
Function of the Frequency
1. Mechanical System Alone
2. Slight Depth of Immersion of Rod in Liquid
3. Deep Immersion of Rod in Liquid

tained with cellulose derivatives, whereas the curve of crepe and especially that of Para rubber show well-defined points of resonance in the range measured. The resonance points indicate elastic forces, and, in conjunction with the fact that the viscosity diminishes with increase in frequency, prove that the particular liquid possesses elasticity.

Figure 24 shows the results of measurements of "resistance to deformation" as a function of the frequency. These results correspond in a qualitative way to the results which would be expected of a Maxwell substance. The characteristically S-form of the curves, in conjunction with the displacement of the resonance points with increasing depth of immersion with higher frequencies, and the crossing of the curves, can be explained only by the fact that the liquid is elastic.

From the experiments described it may therefore be concluded rather safely that under suitable experimental conditions rubber solutions behave in a quite different way from the normal behavior of liquids. On the one hand this conclusion is based merely on viscosity measurements, but on the other hand a good knowledge

of the phenomena involved will suggest other factors and material constants as a means of characterization.

The investigation of all these properties has in general been pursued only recently, and in so far as rubber in particular is concerned, there has been very little experimentation. To what extent this may become of practical importance can be decided only when more experimental facts are at hand.

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The Swelling Capacity of Rubber in Mixtures of Solvents in Relation to Their Dielectric Polarizations

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A wide variety of colloidal processes, especially those which involve organic sols and gels, depend to a great extent on the polar characteristics of the dispersing agent and of the disperse phase, as has been proved by Wo. Ostwald[1] and by various other investigators.

In one of his works,[2] Ostwald proved that the swelling of vulcanized rubber in an organic solvent and the dielectric constant of the solvent are related by a quantitative law, which may be expressed as follows:

$$\sqrt[n]{Q.\epsilon} = K$$

where Q is the number of cc. of liquid absorbed by 100 grams of rubber, ϵ is the dielectric constant of the liquid, n is a factor which varies from 2 to 3, and K is a constant.

The inverse proportionality between the nth root of the swelling capacity Q of the rubber and the dielectric constant of the medium, as shown by this equation, indicates that the swelling of rubber diminishes rapidly with increase in the dielectric constant of the medium.

However, this relationship has been established only in certain cases, e. g., when there is a change of solubility and adsorption with the dielectric constant of the medium. In most cases the relationship can be proved only with the aid of the complex function of dielectric polarization.[3]

Wo. Ostwald has also shown that the course of a colloid chemical process does not have any intimate connection with any particular factor of polarization, e. g., to ϵ, but only with the dielectric molecular polarization $P_{\epsilon m}$, which is a function of ϵ, of the molecular weight, and of the density (Clausius-Mosotti):

$$P_{\epsilon m} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

The study of systems containing mixtures of solvents rather than single organic liquids is of particularly great importance.[4] The behavior of sols (gels) is in this case complicated by the fact that the polar properties of a medium are in most cases not a simple arithmetic mean of the polarizations of the components. As a result of a mutual influence of the molecules, association (polymerization) is possible, and this leads to particles with new polar properties.

The problem is complicated still more by the fact that certain compounds, e. g., water, which is an example of a strongly polar liquid, would be expected to be active with respect to the swelling of substances such as acetylcellulose, as is characteristic of most polar liquids. As a matter of fact, however, water is inactive in this case. On the other hand, when mixed with other solvents, water has the power of greatly activating the latter.[5]

In the light of the investigations of Ostwald,[2] and of LeBlanc and Kröger[6] on the swelling of rubber in pure liquids, and also in view of the complications involved in mixtures of solvents, it seemed of fundamental importance to study the swelling of vulcanized rubber in mixtures of two and even three solvents.

The behavior of vulcanized rubber in various mixtures of water, carbon tetra-chloride, benzene, toluene, nitrobenzene, acetone, ethyl alcohol, and chloroform were therefore studied.

All the binary mixtures were divided, according to their dielectric properties, into four main groups, as follow:

(1)   Mixtures of solvents, both components of which are non-polar:

<div align="center">benzene + carbon tetrachloride</div>

(2)   Mixtures of solvents consisting of a polar and a non-polar component, so chosen that the latter has no influence on the polarization of the former:

<div align="center">
toluene + carbon tetrachloride
toluene + benzene
chloroform + benzene
</div>

(3)   Mixtures of solvents consisting of a polar and non-polar component, so chosen that the latter influences the polarization of the former:

<div align="center">
nitrobenzene + benzene
ethyl alcohol + benzene
ethyl alcohol + carbon tetrachloride
acetone + carbon tetrachloride
</div>

(4)   Mixtures of solvents, both components of which are polar liquids:

<div align="center">
water + ethyl alcohol
acetone + ethyl alcohol
chloroform + acetone
chloroform + ethyl alcohol
</div>

The binary systems were tested in eash case in five different proportions by volume of the two components A and B:

	(1)	(2)	(3)	(4)	(5)
A	1.0	0.75	0.50	0.25	0.0
B	0.0	0.25	0.50	0.75	1.0

Strips of vulcanized rubber 4 cm. long, 1.5 mm. wide, and 1.5 mm. thick were placed in individual glass tubes, 1 cc. of the liquid was added from a microburette to each tube, the tubes were then sealed and kept at 16° C. for 50 hours in a thermostat.

With the aid of a magnifying glass, three measurements of the lengths of the swollen rubber strips were made during the course of the 50-hour immersions, commencing at the end of 24 hours.

Swelling (Q) of Rubber in Solvents of the First Group

Figure 1 shows that rubber swells more in carbon tetrachloride than in benzene. The swelling curve is almost a straight line from one pure solvent to the other.

The change in the swelling capacity of rubber in this particular binary mixture of inactive liquids runs parallel with the change in the molecular polarization of the mixture. Curve P_2 (molecular polarization of the active component) and curve P_{12} (molecular polarization of the mixture) are constructed from the data of Heymann and Boyes.[7]

Swelling (Q) of Rubber in Solvents of the Second Group

Figures 2, 3, and 4 show the swelling in the solvents of the second group. In this group the relation between the polarity of the solvents and the swelling of the rubber is a complicated one.

In the system: toluene + carbon tetrachloride, the P_2 (toluene) values, and the P_{12} (mixture) values change relatively little with change in concentration, P_2 forming a straight line practically parallel with the axis, and P_{12} forming a straight line with an insignificant descent towards higher proportions of carbon tetrachloride. The swelling curve is here roughly parallel to the P_2 curve (Fig. 2).

In Fig. 4, the P_2 curve of the polar component (chloroform) and the P_{12} curve of the mixtures separate with decrease in concentration of the active component (chloroform), and the change in the swelling of the rubber runs parallel with the change in P_2, even to the extent that the maximum P_2 is reflected in a maximum on the swelling curve.

With mixtures of benzene and toluene, the results of which are shown in Fig. 3,

| Figure 1 | Figure 2 | Figure 3 | Figure 4 |
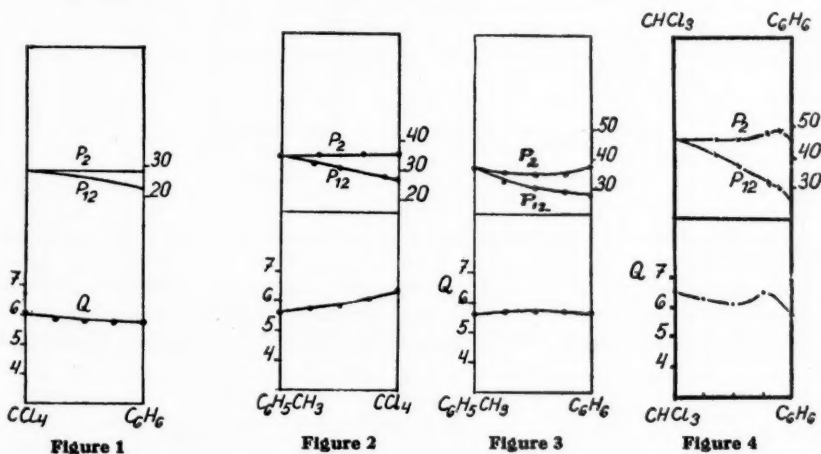
the P_{12} values decrease with decrease in the proportion of toluene, while the P_2 curve shows a slight minimum. On the other hand, the swelling curve shows an ill-defined maximum.

Swelling of Rubber in Solvents of the Third Group

The results of the measurements are shown in Figs. 5 to 8. Characteristic of all the binary mixtures of a polar and a non-polar solvent is the fact that the swelling of the rubber varies inversely with the P_{12} values.

The degree of swelling of rubber is closely related to the polarization of the solvent mixture. However, examination of the curves in Figs. 5 to 8 shows that the trends of the P_2 curves of the polar components deviate markedly from the trends of the swelling curves.

When a P_2 curve has a straight line course, the swelling curve likewise becomes straight in the same direction, whereas the P_{12} curve turns in the opposite direction. Where the P_2 curve shows a kink with a maximum point, this is reflected in the course of the swelling curve, but not in the P_{12} curve. Where there is such a reflection in the swelling curve, it occurs at a point corresponding to the particular mixture of

liquids where the maximum P_2 value for the active components is located.   This influence of the P_2 value was also observed by Heymann and Boye[8] and by Sata and Kurano[9] in the trend of curves of the adsorption of benzoic acid and picric acid on carbon from similar mixtures of solvents.

With regard to the change in the polarization of a polar component with change
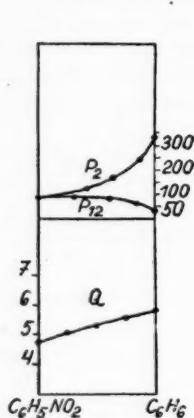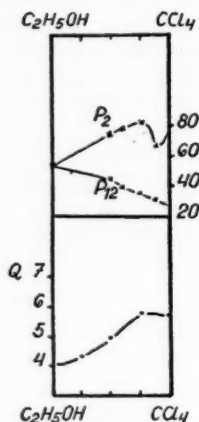
Figure 5   Figure 6

in its concentration in the non-polar solvent, it should be noted that the decrease in the polarization of nitrobenzene (from 340 to 95 cc.) with increase in its concentration in benzene is explained by Debye by an association of nitrobenzene molecules with increase in concentration, since the polar molecules of nitrobenzene are arranged symmetrically in the associated aggregates and thus can form a quadripole.
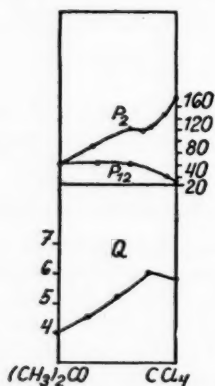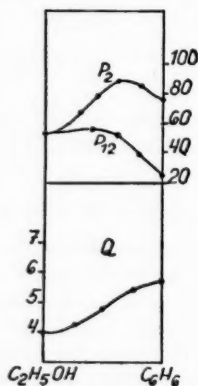
Figure 7   Figure 8

The general tendency for the polarization of polar components to diminish with increase in their concentration is also true of other polar liquids, e. g., ethyl alcohol and acetone (see Figs. 6 and 7), and this must be explained in a similar way.   In the system: benzene + ethyl alcohol, the P_2 curve of ethyl alcohol has a maximum,

which according to the theory of Debye corresponds to a maximum association of ethyl alcohol at this particular concentration in benzene.

Swelling of Rubber in a Mixture of Two Polar Liquids

The results of the measurements are shown in Figs. 9 to 12. The trend of the swelling curves of rubber in mixtures of two polar liquids shows a relatively simple relation to the composition of the mixtures in comparison with the adsorption by carbon in similar media.[10]

In mixtures of highly polar liquids, e. g., water + ethyl alcohol and acetone ethyl alcohol, in which rubber swells to a minimum extent, the swelling of rubber is constant, and is quite insignificant for all proportions of the two ingredients. In mixtures of acetone and ethyl alcohol, there is a slight maximum to the swelling at 75 per cent of acetone.

The linear swelling curve of rubber in mixtures of water and ethyl alcohol corresponds to the linear P_{12} curve derived by Philips[11] for this mixture.

The greater the proportion of the relatively weakly polar chloroform in mixtures of chloroform and acetone and of chloroform and ethyl alcohol, the greater is the swelling of rubber in these mixtures (see Figs. 11 and 12).
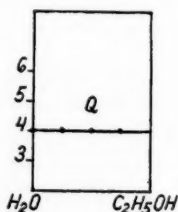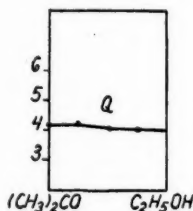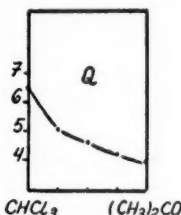
| Figure 9 | Figure 10 | Figure 11 | Figure 12 |
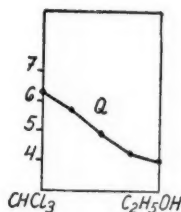
If now the results of the swelling tests of rubber in pure solvents are grouped together, and are compared with the polar constants, as in Table I, it is seen that, aside from a few anomalies, swelling is inversely proportional to the dielectric constants, in conformity with the experiments of Wo. Ostwald.[12]

TABLE I

Solvent	ϵ	$\mu.10^{18}$	P_2	Swelling (Length)
Chloroform	4.95	1.05	46.8	6.46
Carbon Tetrachloride	2.56	0.0	28.1	5.99
Toluene	2.38	0.5	32.7	5.88
Benzene	2.26	0.0	26.3	5.77
Nitrobenzene	34.0	3.9	93.9	4.85
Acetone	21.5	2.6	63.7	4.11
Ethyl Alcohol	25.0	1.7	52.1	4.07
Water	81.0	1.85	..	4.05

Reproduction of the results in a coördinate system, as in Fig. 13, shows that only with chloroform and nitrobenzene are the swelling values off the curve.

This disproportionately great swelling of rubber in chloroform is ascribed by Ostwald to the fact that chloroform decomposes readily in light, and this influences its polar properties. The anomaly in the swelling of rubber in nitrobenzene is attributable to association of its molecules, which leads to a greater symmetry of the aggregate and a diminution in the dipole moment. An anomalous behavior of

chloroform has also been found by Erbing and Sakurada[13] in the coagulation of polystyrene in chloroform by alcohol.

If the swelling of acetylcellulose in organic solvents is compared with that of rubber in the same solvents, it is found that in most cases the greater the polarization of a solvent the more does acetylcellulose and the less does rubber swell in the solvent.

On the other hand, in the important solvents, water and ethyl alcohol, acetylcellulose and rubber swell in a similar way, i. e., each swells very slightly or not at all, and neither dissolves. Accordingly, in spite of the fact that the polarization of the medium governs the swelling, anomalies arising from secondary reactions in the system are to be found.

Swelling of Rubber in Ternary Systems

While studies of the colloidal state in binary solvents were being carried on, more and more attention has recently been devoted to ternary systems. For analyzing these latter systems, the Gibbs triangle method[14] will be found to be useful.

To study the swelling of rubber, the present authors made use of a ternary
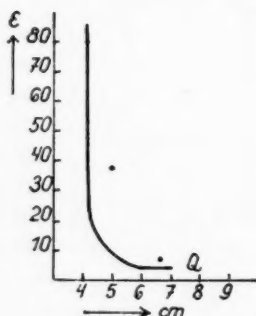
Figure 13
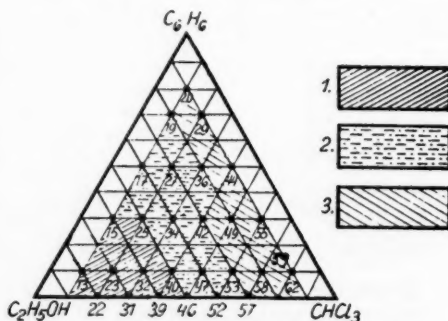
Figure 14

system composed of two polar liquids and a non-polar liquid, viz., ethyl alcohol + chloroform + benzene. Table II summarizes the composition of the various mixtures and the swelling of rubber in the mixtures. The swelling was measured after 8 days' immersion at 13° C.

When these results are plotted in the form of a Gibbs triangle, as in Fig. 14, areas of definite degrees of swelling are obtained. Every point on the triangle corresponds to a definite concentration of all three components. The various shaded areas in the triangle correspond to one length of the rubber strip:

(1) 4 to 5 cm.
(2) 5 to 6 cm.
(3) over 6 cm.

As is obvious from the diagram, the swelling of the rubber increased with increase in the proportions of benzene and of chloroform in the mixture.

The smallest area of any of the three shaded areas on the triangular diagram comprises the region of minimum swelling, which is governed by the component with the greatest polarization, i. e., ethyl alcohol.

If the data in Table II are compared with corresponding data on the swelling

TABLE II

SWELLING OF RUBBER IN THE SYSTEM: ETHYL ALCOHOL–CHLOROFORM–BENZENE

| No. of the Points | Components | | | Length (Cm.) |
	Ethyl Alcohol (Cc.)	Benzene (Cc.)	Chloroform (Cc.)	Original Length (4 Cm.)
1/13	0.8	0.1	0.1	4.32
2/15	0.6	0.3	0.1	4.70
3/17	0.4	0.5	0.1	5.20
4/19	0.2	0.7	0.1	5.92
5/20	0.1	0.8	0.1	6.20
6/22	0.8	...	0.2	4.25
7/23	0.7	0.1	0.2	4.45
8/25	0.5	0.3	0.2	4.88
9/27	0.3	0.5	0.2	5.60
10/29	0.1	0.7	0.2	6.25
11/31	0.7	...	0.3	4.40
12/32	0.6	0.1	0.3	4.62
13/34	0.4	0.3	0.3	5.25
14/36	0.2	0.5	0.3	6.00
15/39	0.6	...	0.4	4.65
16/40	0.5	0.1	0.4	4.90
17/42	0.3	0.3	0.4	5.65
18/44	0.1	0.5	0.4	6.35
19/46	0.5	...	0.5	4.92
20/47	0.4	0.1	0.5	5.25
21/49	0.2	0.3	0.5	6.05
22/52	0.4	...	0.6	5.32
23/53	0.3	0.1	0.6	5.75
24/54	0.2	0.2	0.6	6.10
25/55	0.1	0.3	0.6	6.45
26/57	0.3	...	0.7	5.75
27/58	0.2	0.1	0.7	6.15
28/59	0.1	0.2	0.7	6.50
29/61	0.2	...	0.8	6.15
30/62	0.1	0.1	0.8	6.50
31/64	0.1	...	0.9	6.55

(1) Region of 4 to 5 cm.
    Points 13, 15, 22, 23, 25, 31, 32, 39, 40, 46.
(2) Region of 5 to 6 cm.
    Points 17, 19, 27, 34, 42, 47, 52, 53, 57.
(3) Region over 6 cm.
    Points 20, 29, 44, 49, 54, 55, 58, 59, 61, 62, 64.

TABLE III

BINARY SYSTEM: BENZENE–CHLOROFORM

| Components | | Swelling (Length) of the Rubber Strip |
Benzene (Cc.)	Chloroform (Cc.)	(Cm.)
0.75	0.25	5.87
0.50	0.50	6.05
0.25	0.75	6.29
0	1.0	6.46

TABLE IV

TERNARY SYSTEM: BENZENE–CHLOROFORM–ETHYL ALCOHOL

| Components | | | Swelling |
Benzene (Cc.)	Chloroform (Cc.)	Ethyl Alcohol (Cc.)	(Cm.)
0.7	0.2	0.1	6.25
0.5	0.4	0.1	6.35
0.2	0.7	0.1	6.50
...	0.9	0.1	6.55

in binary mixtures, as shown in Table III, it is evident that the addition of 0.1 cc. of ethyl alcohol to a mixture of benzene and chloroform brings about considerable increase in the swelling, whereas the swelling in ethyl alcohol itself is insignificant. This is shown in Table IV.

A similar phenomenon in a binary system was observed by Wo. Ostwald and Ortloff.

Résumé

1. The swelling of vulcanized rubber is a simple function of the polarization of the solvent.

2. The swelling curve of rubber in mixtures of two apolar solvents (1st group) shows a parallelism with the P_{12} curve (Fig. 1).

3. With a mixture of two polar solvents (4th group), where the P_{12} value of the mixture is known, $e.\,g.$, water $+$ ethyl alcohol, the swelling curve of rubber runs parallel with the P_{12} curve. With mixtures of polar solvents with undetermined P_{12} values, the swelling curves are nearly straight lines, which correspond to the arithmetic means of the pure components. In Figs. 11 and 12, however, slight minima are evident.

4. In a mixture of two solvents, the apolar of which influences the polar (3rd group), the swelling curve follows a different direction from that of the P_{12} curve (Figs. 5 to 7). Mixtures of benzene and ethyl alcohol are an exception to this rule. The trend of the swelling curve of rubber in these mixtures of solvents reflects the course of the P_2 curves of the active components (Figs. 6 and 7).

5. It is difficult to establish any general rules for mixtures of solvents of the 2nd group. When the apolar component appears to have an active swelling power (carbon tetrachloride, see Fig. 2), this component brings about an analogous trend of the swelling curve of rubber in solvents of the 3rd group. In the system: benzene $+$ chloroform (Fig. 4) the swelling curve of rubber runs parallel to the P_{12} curve. The system: benzene $+$ toluene, shows an intermediate state (Fig. 3).

6. Data on the swelling of rubber in ternary mixtures of solvents are described. When added to a mixture of benzene and chloroform, inactive but polar ethyl alcohol increases greatly the swelling of rubber. The region of minimum swelling is the smallest area on the Gibbs triangle, and represents the influence of the component with the greatest polarization, $viz.$, ethyl alcohol.

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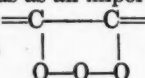
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Various Ozonides of Rubber and the General Question of the Existence of Primary Ozonides
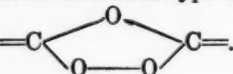
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Harries was the first to make use of ozone cleavage at the carbon double bond of unsaturated compounds as an important method of research in organic chemistry. However, the formula $\begin{smallmatrix} =C\text{---}C= \\ | \quad\ | \\ O\text{---}O\text{---}O \end{smallmatrix}$ of Harries, which is founded on its analogy with the products of other addition reactions, rests on scanty experimental data. One of the chief arguments against the formula is the absence of glycols as reaction products by the action of the most varied types of reducing agents. This latter fact, in conjunction with certain polymerization phenomena, led Staudinger to propose an isoozonide type of formula, in which the carbon chain has been opened,

thus $=C\underset{O\text{---}O}{\overset{O}{\diagdown\hspace{-0.3em}\diagup}}C=$.

According to Staudinger, these isoozonides are formed very readily by transposition from primary or molozonides, and they are stable compounds. On the contrary, some molozonides are stabilized by polymerization. The constitution of butylene ozonide was proved synthetically by Rieche and Meister to be that of an isoozonide, and today the isoozonide formula has received general acceptance.

In spite of these facts, some of the results of Harries, on which he based his original ozonide formula, remain unchallenged; for instance, the fact that when heated the ozonide of mesityl oxide reverts to mesityl oxide, and the fact that fumaric acid forms with ozone a loose compound from which ozone is liberated easily. In view of this, it appeared as if the Harries formula would really turn out to be the correct one, and that stable molozonides should exist.

Experiments carried out by the present author in collaboration with Matthäus on rubber and on gutta-percha also have pointed to the existence of molozonides (cf. *Angew. Chem.*, **47**, 366 (1934)). In view of this, the present author, with the aid of Hermann Richtzenhain, studied more thoroughly the behavior of rubber in this respect, as well as the fundamental experiments of Harries. The results of this work are discussed in the present paper.

Attempts to decompose the ozonide of mesityl oxide into appreciable amounts of mesityl oxide under the conditions described by Harries were unsuccessful. In two experiments normal cleavage fragments were obtained; and two more experiments led to explosions, one of which was extremely violent. Further experiments were therefore abandoned. Nor with fumaric acid was it found possible to split off ozone from its ozonide; in fact it was found that in general fumaric acid reacts with ozone only with great difficulty, so that the fumaric acid recovered from a solution treated with ozone is in all probability fumaric acid which has not reacted, rather than fumaric acid regenerated by decomposition of its ozonide.

With ethyl fumarate, a crystalline ozonide was obtained, cleavage of which by reduction yielded ethyl glyoxalate in quite a normal way, but no tartaric acid. Consequently, in both these cases the isoozonide formula explains in a satisfactory manner the course of the reactions.

It had been found, as mentioned above, that treatment of chloroform solutions of rubber and gutta-percha with ozone does not decrease the bromine titer of the solutions, as would be expected if the ozone combined at the double bonds. Normal
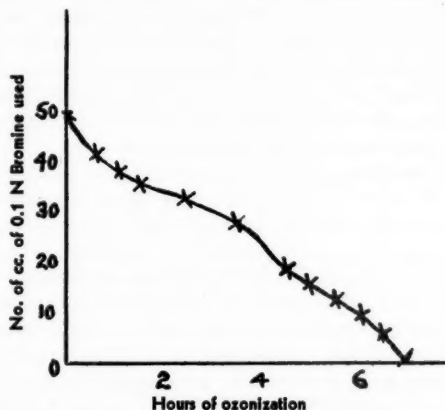
Figure 1—Ozonization of Amylene

curves such as would be expected are on the other hand obtained with amylene (see Fig. 1), isoheptene, and mesityl oxide.

In the case of rubber, the bromine titer remains practically constant almost to the completion of the ozonization, and then suddenly diminishes to zero (see Fig. 2). This drop occurs within a few minutes during addition of the last 2 per cent of ozone, in fact, perhaps, only by addition of excess of ozone. This drop in the bromine titer commences at the "critical point," when ozone is detected in the
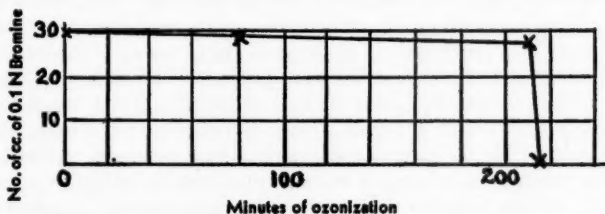
Figure 2—Ozonization of Sol Rubber in Chloroform at 0° C.

solution by means of potassium iodide. Two years ago, however, it became evident to the present author that perhaps bromine does not displace the ozone combined at the double bonds, but that the ozonide ring systems of the primary-ozonide render the molecule particularly susceptible to substitution by bromine. Since then we have been able to identify the location where bromine enters the molecule as a substituent, viz., in the CH_2 group which is attached to the same carbon atom as is the methyl group, as shown below.

$$-CH_2-C\overset{CH_3}{\underset{O-O}{\diagup}}O\diagdown CH-CH_2- + Br_2 \longrightarrow -CHBr-C\overset{CH_3}{\underset{O-O}{\diagup}}O\diagdown CH-CH_2- + HBr$$
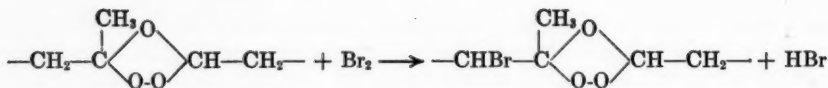
This is followed by substitution in the methyl group itself. On the contrary the hydrogen on the double bond is hardly attacked. Under no conditions was levulinic aldehyde, or levulinic acid obtained as a result of cleavage by reduction of the brominated primary ozonide, and β-bromolevulinic acid and β,δ-dibromolevulinic acid were the only products. These are the same products obtained by Harries as a result of the action of bromine on the final ozonide for many hours.

With the primary ozonide, these two products are formed as rapidly as a titration can be carried out, and only in this sense can the final ozonide be regarded as stable to bromine, *i. e.*, for intervals of several minutes (up to 10). As is well known, on longer standing this ozonide also consumes bromine slowly.

There now comes the problem as to how many ozonides of rubber warrant being called by this term. If, following the method of Harries, an ozonide is prepared from sol rubber in chloroform solution at 0° C., with interruption of the reaction at the "critical point," and if the reaction product is then concentrated in a vacuum, dissolved in ethyl acetate, precipitated with petroleum ether, and the precipitation repeated several times, there is obtained an ozonide which solidifies to a vitreous mass of almost exactly the composition, $(C_5H_8O_3)_x$, *i. e.*, quite normal. Sensitivity to bromine does not involve a low oxygen content. This ozonide softens at 35° C., and at 45° C. it commences to decompose, with evolution of gas. It is insoluble in ether, petroleum ether, carbon tetrachloride; more readily soluble in benzene and acetone, and easily soluble in acetic acid, ethyl acetate, and dioxan.

Neither the solubility nor the empirical composition is altered when the product is treated with ozone for a few minutes longer, *i. e.*, until the stability to bromine suddenly diminishes. The primary ozonide which is separated and reprecipitated shows a varying consumption of bromine, reaching as high as 91 per cent of that calculated for rubber. Cryoscopic determinations of the molecular weight of the primary and of the stable ozonide in bromoform gave a value of 580, which corresponds to $(C_5H_8O_3)_5$, whereas Harries, working with benzene, obtained a lower value corresponding to $(C_5H_8O_3)_4$.

A hitherto unknown, difficultly soluble rubber ozonide can be obtained in carbon tetrachloride. Harries reported that no ozonide precipitated from this solvent, and that the appearance of a precipitate is evidence of the presence of rubber resins. In spite of this, in the present work ozonides were precipitated both from crepe rubber and from sol rubber. From the point of view of kinetics, these reactions are interesting because, with the introduction of only 60 per cent of the calculated quantity of ozone, an ozonide of normal composition was obtained, which analyzed pure after being washed and freed of carbon tetrachloride in high vacuum. The precise analytical results indicate that to a predominant extent a molecule, when once oxidized, reacts completely, rather than that the ozone available distributes itself uniformly on all the molecules of rubber. The yields of precipitated ozonide, based on the ozone introduced, amounted to 67 per cent of the theoretical value. In addition to this yield, there was recovered from the solution 15 per cent of unaltered rubber containing 3 per cent of oxygen, the presence of which may have been due to dissolved ozonide. The ozonide prepared in this way with a deficiency of ozone softened only at 75° C., and commenced to decompose at 85° C. In distinction to the ozonide prepared in chloroform, this ozonide is much more difficultly soluble in chloroform, benzene, and ethyl acetate. Furthermore in most cases it

corresponded to a bromine consumption of only 19 per cent of the theoretical value (based on the rubber), *i. e.*, in spite of the relatively small proportion of ozone used (60 per cent), the ozonide is thoroughly "stabilized." In view of its low solubility and rapid precipitation, one may assume that it is but slightly degraded, *i. e.*, it is of relatively high molecular weight. Equally surprising is the fact that a cryoscopic determination of the molecular weight in bromoform gave a value of 580, *i. e.*, the same as that of the ozonide in chloroform. This is plainly evidence of further decomposition of the ozonide in these solvents. The remarkable fact had already been established that on long standing, *i. e.*, 10 to 14 days at 0° C., solutions of the ozonides in chloroform undergo still further decomposition, with precipitation of levulinic acid peroxide, while the ozonide remaining in solution becomes soluble in ether. This decomposition product cannot be regarded as a rubber ozonide, for rubber ozonides are insoluble in ether.

The ozonide, which gives a clearly defined quintuple composition by analysis, corresponding to the formula $(C_5H_8O_3)_5$, can be represented in three different ways with various end groups.

(1) $\underset{O}{\overset{H}{>}}C-CH_2-\left(CH_2-\underset{\underset{O-\!-\!-O}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH-CH_2 \right)_4-CH_2-C\underset{O}{\overset{CH_3}{\diagup}}\underset{O}{\diagdown}$ an aldehydeketone peroxide

(2) $HO_2C-CH_2-\left(CH_2-\underset{\underset{O-\!-\!-O}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH-CH_2 \right)_4-CH_2-\overset{\overset{CH_3}{|}}{C}=O$ a ketone acid

(3) $\underset{O}{\overset{O}{>}}CH-CH_2-\left(CH_2-\underset{\underset{O-\!-\!-O}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH-CH_2 \right)_4-CH_2-\overset{\overset{CH_3}{|}}{C}=O$ an aldehyde peroxide ketone
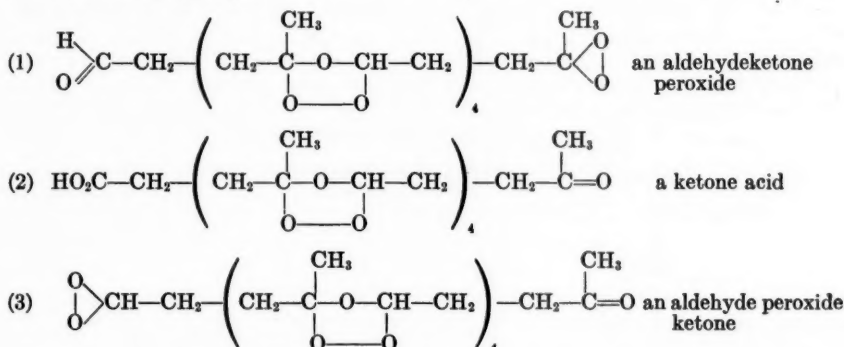
The problem then arises as to the way in which the primary ozonide, which is sensitive to bromine, differs from the final stable product, which has been over-ozonized for a few minutes. Two years ago it was assumed that the product which is sensitive to bromine is a "primary ozonide" of the type represented by the Harries formula, and that it is transformed by traces of excess ozone into the stable iso-ozonide. This point of view, which because of the rapidity of the transformation during only a few minutes of ozone treatment has much in its favor, does not today seem to be correct. In fact the most careful experiments on the reduction of the relatively stable "primary ozonide" by aluminum amalgam and by zinc dust gave no polyglycol, which would necessarily be formed from the ozonide of Harries, but only normal decomposition products instead. Accordingly in this reduction also, the previous "rearrangement" must be accepted as a working hypothesis.

The number of "rearranging" agents is however extremely limited, as becomes evident from the many experiments carried out in the present investigation. In addition to ozone, perbenzoic acid has been found to be effective, whereas hydrogen peroxide is relatively very inactive, and benzoyl peroxide and halogens are wholly inactive. The assumption of a final saturation of a residual terminal double bond (perhaps conjugated) in the very long rubber chain does not explain the facts at all satisfactorily. This is particularly true in view of the fact that in the chloroform solution which was tested for its stability to bromine, the rubber ozonide was already decomposed into residual fragments containing only 25 carbon atoms.

A more reasonable concept seems rather to be that perbenzoic acid, even 3 per cent of which (based on the original rubber double bonds of the ozonide) has a noticeable effect, acts as a negative catalyst of bromine substitution, in spite of the
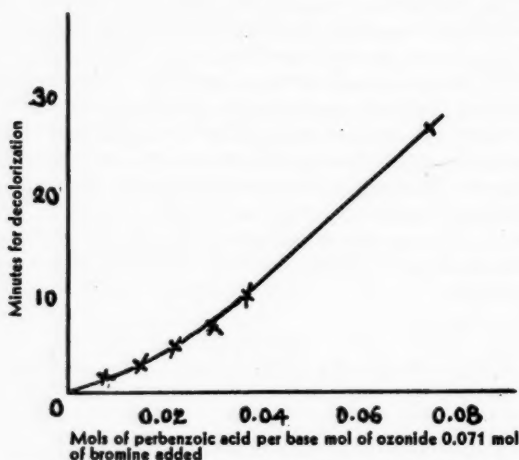
Figure 3—Retardation of the α-Bromination of Rubber Ozonide by Perbenzoic Acid
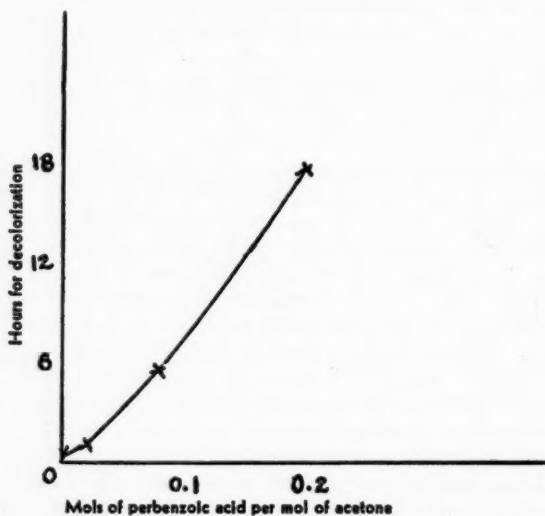
Figure 4—Retardation of the Bromination of Acetone by Perbenzoic Acid

fact that many cases are known where perbenzoic acid acts as a positive catalyst and accelerates bromine substitution through the agency of hydrogen bromide.

Figure 3 shows the influence of various concentrations of perbenzoic acid on chloroform solutions of the primary ozonide + 0.07 mol of bromine. This quantity

of bromine, which is decolorized immediately in the absence of perbenzoic acid, remains visible for 10 minutes in the presence of 0.037 mol of perbenzoic acid. A still greater retarding action is exerted by perbenzoic acid when the bromination is carried out in acetone. With 0.05 mol of bromine and 0.2 mol of perbenzoic acid per mol of acetone, the color of the bromine remains visible for 18 hours, and with 0.02 mol of perbenzoic acid it remains for 80 minutes (see Fig. 4).

In view of these control experiments, all that is necessary to explain the sudden "rearrangement" of the primary ozonide by a very slight excess of ozone is to assume, for example, that the aldehydeozonide of Formula (1) above is transformed into a peracid, which then, even in very small concentrations, has just as great a retarding action on the bromination as does perbenzoic acid. Whether the ozonide which is formed in carbon tetrachloride with a deficiency of ozone also contains any peracid is of course an unsettled question. Possibly it is a polymeric ozonide with higher ring systems, e. g., ten rings instead of five rings, which activate the neighboring CH_2 groups to a less extent. The primary rubber ozonide shows in fact a particularly great reactivity toward bromine, which was not found to be true either of the ozonide of amylene or of the ozonide of isoheptene, in spite of similar branchings on the double bonds. Evidently the aggregation of several ozonide groups in the molecule, as in the case of rubber and also of gutta-percha, also plays a part in the phenomenon.

The retarding action of perbenzoic acid can be explained perhaps by the fact that bromination is a chain reaction in which perbenzoic acid has the power of breaking the chain by removing a trivalent carbon radical, which functions as a link in the chain. The retarding action of perbenzoic acid is not limited to the bromination of rubber ozonide and acetone, and its retarding effect on the addition of bromine to ethyl acetate is an excellent lecture experiment.

The Infrared Absorption of Rubber and Related Hydrodcarbons

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The infrared absorption spectra of rubber and certain related hydrocarbons have been studied by using extremely thin films of the samples as absorbing layers. In the spectra of styrene, isoprene, and cymene intense absorption bands appear at 3.4μ, 6.2μ, and 7.0μ and also weaker bands between 7μ and 9μ. These bands were common to most of the hydrocarbons studied. The principal variations in the spectra of the compounds mentioned above are found in bands whose positions vary between 5.5μ and 5.7μ in the different compounds. In the case of "pure gum" rubber a band was found at 5.8μ and in a vulcanized rubber of low sulfur content corresponding absorption occurs at 6.0μ. At all other wave-lengths between 2.5μ and 9.0μ the absorption spectrum of rubber has a striking resemblance to that of isoprene, a result which is in agreement with the chemist's model of the rubber molecule as a long chain of isoprene units. The absorption in the 5.8μ region probably arises from a mechanism which is intimately connected with the process of polymerization. The spectrum of polymerized butadiene contains strong bands at 5.5μ and 6.0μ and also less intense bands beyond 7.0μ, whose positions are not the same as those in the spectrum of natural rubber. Rubber hydrochloride has a very intense band at 8.4μ which is not characteristic of the other hydrocarbons studied.

Roentgenographic Investigations of Stretched Vulcanized Rubber

Morihiro Iguchi and Fritz Schossberger

Ordinary unvulcanized rubber and cold-vulcanized rubber show, when not stretched, an amorphous x-ray spectrum composed of a single ring with an identity period of 4.9 A. U.[1] When rubber is stretched, crystal interferences appear as soon as its elongation exceeds 75 per cent.[2] Since all the crystals lie with their crystallographic direction parallel to the fibre axis, not only is a crystal diagram obtained but also a fibre diagram.

When such elongated rubber retracts, the amorphous diagram reappears. In order to explain this behavior of stretched and unstretched rubber, Katz[1] assumed that the crystalline substance in the rubber is formed only during stretching. On the other hand, Gerngross, Herrmann, and Lindemann[3] believe that a crystalline phase is already present before stretching, but that the crystallites are too small and the disarrangement of the lattice is too great for the crystalline phase to be visible in the x-ray diagram. The changes in the intensity of the interferences with change in elongation were studied by Mark and Hauser.[4] Their work proved that only when the elongation reaches 80 per cent does an appreciable intensification appear. Below this critical elongation no crystal interferences are in general evident.

Above 80 per cent elongation, however, the intensity of the (110) interference is a linear function of the elongation. The higher orders reach their maximum intensities only at higher elongations; in other words, the crystals which are formed acquire a regular structure only at the higher elongations. On the other hand, the amorphous ring diminishes as an inverse linear function of the elongation.

The axes of the rhombic unit substance in stretched rubber have been studied by Mark and von Susich,[5] and the arrangement of the molecules in the unit substance by Meyer and Mark.[6] In this work it was assumed that the molecular chains formed by polymerization of isoprene penetrate the cells in such a way that the unit substance indicated by roentgenographic analysis is much shorter than the individual molecule.

The chief aim of the experiments described in the present paper was to obtain more information on the state of vulcanized rubber before it is stretched. In other words, it was hoped to ascertain whether the amorphous ring is changed by elongating rubber, and if so, in what way.

To explain the elastic properties of rubber, Meyer, von Susich, and Valko[7] assumed that very long oriented primary valences are present in rubber when the latter is in the stretched state. The amorphous ring of unstretched rubber indicates an average distance of approximately 4.9 A. U. The simplest though not the only possible basis for assuming this distance is the fact that it is identical with the average distance of the individual fiber molecules from one another. More precise data can be obtained by means of the Fourier method of analysis, which has actually been carried out by Simard and Warren[8] subsequent to the conclusion of the work described in the present paper. Fourier analysis gives a distribution curve of the number of carbon atoms lying at any distance whatsoever from a given carbon atom. The first maximum of this curve lies at 1.5 A. U. and the second maximum at 2.6 A. U.

The state of rubber before crystallization is of particular interest in connection with the work of Guth and Mark[9] on the static effect during the stretching of rubber.

Experimental Results

Attention should be called to the fact that the results described in the present paper are not directly comparable with the results of Mark and Hauser,[4] particularly with regard to the critical elongation, because, as already mentioned, the work in the present paper is concerned with vulcanized rubber.

The rubber employed was the same as that employed by Ornstein, Wouda, and Eymers[10] for their thermodynamical investigations,[13] and was of the following composition:

First latex sheet	100
Sulfur	5
Diphenylguanidine	1
Zinc oxide	3

When strips of this vulcanizate, 8 mm. wide, 20 mm. long, and 1 mm. thick, were stretched step by step in 10 per cent increases, no crystal interferences appeared in the x-ray diagram, even at an elongation of 250 per cent. Only at about 260 per cent elongation attained by stepwise stretching did crystal interferences become visible and grow more intense at higher elongations.
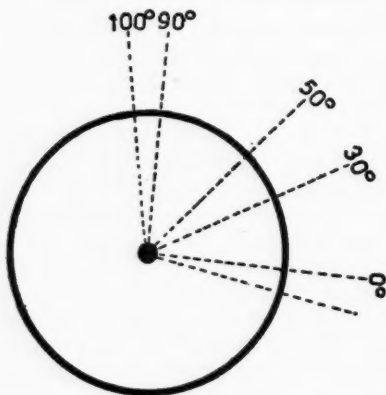
Figure 1

When rubber was not stretched step by step but was stretched directly to 260 per cent, the crystal interferences became visible immediately. When the stretched rubber was allowed to retract slowly, the crystal interferences remained visible down to an elongation of 130 per cent, from which point they became weaker, and finally passed over into an amorphous ring at an elongation of 100 per cent (see Table I).

When four different samples of rubber were stretched directly to 100, 150, 200, and 250 per cent, respectively, only an amorphous ring was obtained up to 200 per cent (see Table II).

TABLE I

RETRACTION OF RUBBER

(Sample No. 2, Distance 4 Cm., 4 Hours, 45 Kv., 14 Milliamp.)

No.	Percentage Elongation	Interferences
26	260	Crystal interferences
27	240	Crystal interferences
28	200	Crystal interferences
29	150	Crystal interferences
34*	100	Amorphous ring
30	80	Amorphous ring

TABLE II
STRETCHING OF RUBBER
(Samples Nos. 3, 4, 5, and 6)

No.	Sample No.	Percentage Elongation	Effect
55	3	250	Crystal interferences
35*	4	200	Amorphous ring
32	5	150	Amorphous ring
31*	6	100	Amorphous ring

Film No. 25
Figure 2

Film No. 31 ———, 34 - - - - -
Figure 3
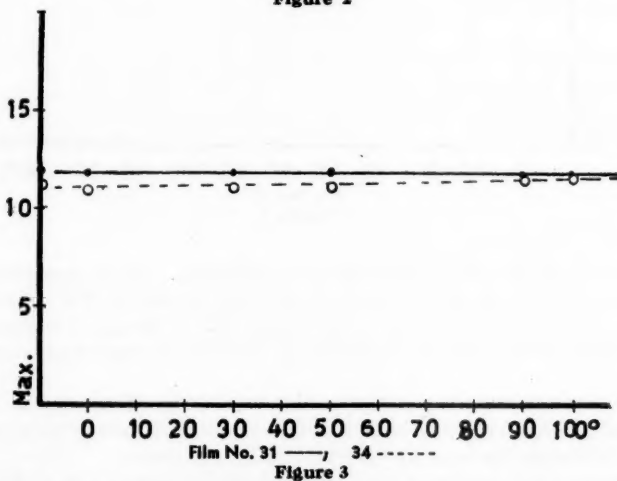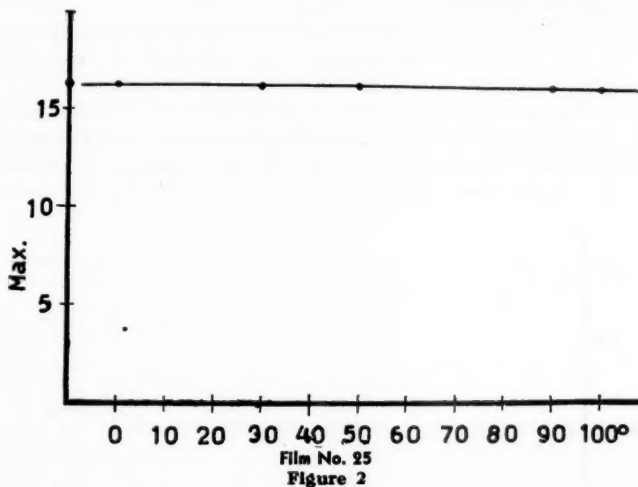
To follow the changes in intensity in the x-ray diagrams, photometric measurements were made in a few cases (marked by asterisks in the tables), as follow:

No. 25   Elongation 0 per cent (Fig. 2).
31   Elongation 100 per cent (Table II, Fig. 3).
34   Stretched to 250 per cent; then slowly released to 100 per cent and irradiated (Table I, Fig. 3).
35   Elongation 200 per cent (Table II, Fig. 4).
26   Elongation 260 per cent.

The measurements were so planned that in all cases a radial sector of 110° was photographed in six directions, a method which had previously been applied successfully to the study of cellulose esters[11] (see Fig. 1).

The photometer was a photoelectric recording instrument with a slit 1.01 mm. long and 0.0094 mm. wide. All the x-ray diagrams were obtained with the same time of exposure, and were developed in the same way so that sources of errors in measuring the intensity maxima were avoided within the variations of intensity of the roentgen tubes.

In the diagrams shown, the abscissae represent the angles through which the photometer slit has passed on the diagram; the ordinates represent the intensity maxima after allowing for the blackening of the background.

In Fig. 2 the points measured for unstretched amorphous vulcanized rubber are recorded. These necessarily form a straight line parallel to the abscissa.

In Fig. 3 the solid line represents a sample which had been stretched directly to 100 per cent. It is obvious that, to the point of a diminution in intensity, there is

Film No. 35
Figure 4
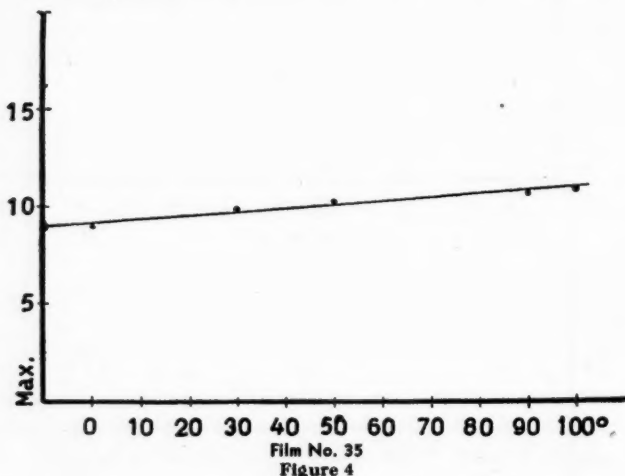
no difference between this and the preceding diagram. On the contrary, the broken line represents a sample which was first stretched directly to 260 per cent, and was then allowed to retract slowly in the course of several days to 100 per cent elongation. A slight diminution in the intensity towards the photometric angle of 0° is evident.

Finally Fig. 4 represents a sample which was stretched directly to 200 per cent elongation. The intensity maxima shows in general still lower values, and the slope of the line through the measured points on Fig. 4 is steeper.

Considering the behavior of unvulcanized rubber, it was also to be expected in the present case that during the retraction of vulcanized rubber the crystal interferences would remain until the elongation had diminished below the critical point. As seen in Table I, this was found to be true.

Finally it is evident from Fig. 3 that the intensity in the amorphous ring does not diminish proportionately, but shows evidence of a hysteresis effect, which results in two x-ray diagrams which differ in intensity diminution, according to whether 100 per cent elongation is reached by stretching or by retraction.

When, as in the past, it was assumed that in stretching rubber, crystallites form in an orderly fashion above the critical elongation, it seemed probable that even before reaching the critical elongation, conditions were favorable for the formation of crystallites. This expectation is substantiated by the x-ray diagram represented in Fig. 4. The effect is therefore to be explained on the basis that, during stretching, the molecular chains assume in part a parallel arrangement.

In further work, it is planned to obtain roentgenographs with monochromatic radiation and in a vacuum, and it is also planned to undertake a Fourier analysis of vulcanized rubber stretched below its critical elongation.

Summary[14]

The intensity of the amorphous ring of vulcanized rubber does not diminish uniformly in all parts of the ring with increase in the elongation, but diminishes from the equator towards the meridian. This effect indicates the existence of a hysteresis phenomenon.[12]

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[12] Katz (*Gummi-Ztg.*, **41**, 2091 (1927)) has found qualitatively a similar intensity distribution in the amorphous ring of stretched highly vulcanized rubber.

[13] The kindness of Dr. A. van Rossem of the Rijksrubberdienst of Delft, Holland, in furnishing this sample of rubber is gratefully acknowledged.

[14] The gratitude of the authors to E. Guth and O. Kratky for their interest and valuable advice is acknowledged here. Thanks are also due Professor H. Mark for so kindly granting the authors the privileges of the Institute of Chemistry at his University.

The Structure of Synthetic Types of Rubber.   Polychloroprenes

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Ozonization is one of the most successful and most exact methods for determining the structure of rubber.   It was this method which was first used by Harries[1] and his numerous collaborators for determining the structures of various types of natural and synthetic rubbers.

By ozonizing solutions of natural rubber, Harries obtained ozonides, the decomposition of which yielded levulinic acid and levulinic aldehyde.   This was proof that the combination of isoprene residues in the rubber molecule is in the 1,4-1,4 position, and it also showed the nature of the base molecules of rubber and the manner in which they are united in chain formation.   On the other hand, these investigations did not give any decisive evidence as to whether the rubber molecule is an open chain or has a ring structure.

At the beginning of his investigations in this field, Harries assigned to the hydrocarbon which is the fundamental constituent of the rubber molecule the following formula:

$$H_3C-C----CH_2$$
$$CH \quad CH_2$$
$$CH_2 \quad CH$$
$$-CH_2-C-CH_3$$
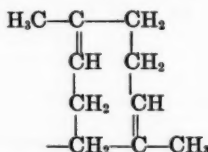
Nothing was said at the time about the size of the rubber molecule.   Later Harries expressed the opinion that a larger ring must exist in the molecule, though its size was not established.

According to the most recent views on the structure of rubber, which are based on determinations by physico-chemical methods, the rubber molecule is considered to be built up as follows:

$$-CH_2-C=CH-CH_2-(CH_2-C=CH-CH_2)_x=CH_2-C=CH-CH_2-$$
$$CH_3 \qquad CH_3 \qquad CH_3$$
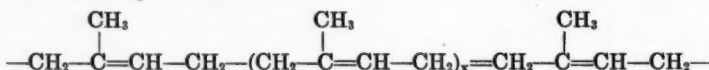
According to evidence obtained by Staudinger,[2] this molecule may contain up to 2000 isoprene units.   To determine the molecular weight and the structure of the rubber molecule, Pummerer[3] resorted to purely chemical methods.   To this end he attempted to isolate the end groups of the rubber chains, which necessarily differed from the inner groups, and then to determine them quantitatively.   In the case of structure I (below) ozonization would, according to this view of Pummerer, necessarily give acetone, levulinic aldehyde, malondialdehyde, methylglyoxal, and formaldehyde:

$$CH_3 \qquad CH_3 \qquad CH_3$$
$$H_2C-C=CH-CH_2-(CH_2-C=CH-CH_2)_n-CH_2-C=CH-CH_2-CH=$$
$$CH_3$$
$$C-CH=CH_2-$$

(I)

In the case of structure II (below) ozonization would give acetaldehyde, levulinic aldehyde, acetoacetic aldehyde, methylglyoxal, and formaldehyde:

$$H_3C—CH=\overset{\overset{\displaystyle CH_3}{|}}{C}—CH_2—(CH_2—CH=\overset{\overset{\displaystyle CH_3}{|}}{C}—CH_2)_n—CH_2—CH=\overset{\overset{\displaystyle CH_3}{|}}{C}—CH_2—CH=$$
$$\overset{\overset{\displaystyle CH_3}{|}}{CH—C}=CH_2 \tag{II}$$

Although Pummerer did not succeed in isolating these end products, he nevertheless believed that the problem might be solved by further methodical experimentation. This conclusion is probably unwarranted, however, since with the high molecular weight of rubber (100,000–120,000 or more) the end groups cannot be determined by ordinary chemical methods. As a matter of fact, this is substantiated by the work of Pummerer.

The elaboration of the ozonization method by Pummerer and his almost quantitative results show conclusively that rubber is built up of isopentene base molecules.

$$—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{C}=CH—CH_3 \tag{III}$$

For synthethic chloroprene rubber, Carothers[4] has established the following formula:

$$—CH_2—\overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}=CH—CH_2—CH_2—\underset{\underset{\displaystyle Cl}{|}}{C}=CH—CH_2—CH_2—\underset{\underset{\displaystyle Cl}{|}}{C}=CH—CH_2—$$

This formula, which is analogous to the formulas of natural rubber and of normal synthetic rubber, is confirmed in three ways: (1) the formation of succinic acid by the oxidation of chloroprene rubber by nitric acid; (2) the stability of the chlorine in the molecule towards alkalies, and (3) certain physical properties, such as the molecular refraction. Carothers proved further that, depending on the conditions under which polymerization is carried out, chloroprene polymerizes to various types of polymers, among which the α-, μ-, and ω-polymers are particularly worthy of mention.

The α-polymer of chloroprene is a soft, plastic mass, soluble in chloroform, carbon tetrachloride, benzene, xylene, and chlorobenzene, and, according to observations of the present authors, almost insoluble in diethyl ether, ethyl acetate, benzine, and petroleum ether. Its properties remind one of those of unvulcanized rubber. Unless it is stabilized, this α-polymer changes spontaneously into the μ-polymer, which corresponds to normal vulcanized rubber. The μ-polymer is an elastic, very firm mass, which does not dissolve in chloroform, carbon tetrachloride, carbon disulfide, benzene, nitrobenzene, pyridine, aniline, ethyl acetate, or diethyl ether, but does swell greatly in these liquids. Many of the properties of the μ-polymer, e. g., its elasticity and its tendency to swell, depend to some extent on the conditions of its preparation.

According to observations of the present authors, the μ-polymer is transformed by the prolonged action of chloroform in the presence of air into the chloroform-soluble modification. About two months are required for this transformation to take place. The μ-polymer is also transformed into the soluble modification by brief treatment with ozone in a proportion far too small to bring about ozonization.

Carothers is of the opinion that the μ-polymer is composed of three-dimensional macromolecules, which are formed by linking of fiber molecules of the α-polymers

by a chemical reaction. This linking of the fiber molecules takes place, of course, only at a few points.

The third type of polychoroprene, the ω-polymer, is distinctly different, both in appearance and properties, from the α- and μ-polymers. It has a granular structure and is formed by polymerization of chloroprene in the presence of various metals or of some of the ω-polymer itself; it is also formed autocatalytically, as was found by Carothers, and as has been verified several times by the present authors. The ω-polymer is neither plastic nor elastic, and it is not only insoluble in all known solvents but swells only slightly in the latter.

The differences between the individual polymers may arise either from differences in their base molecules or from differences in the manner in which these base molecules are linked together.

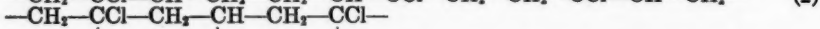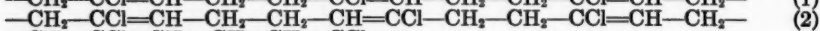In view of this, the present authors undertook the problem of determining the parent members and the manner in which they are linked together. To this end the ozonization method was chosen, since it is the method which has given the most enlightening results in investigations of unsaturated high-molecular compounds. It also makes possible an answer to the question as to the manner in which the base molecules are linked together.

The macromolecules of a polychloroprene can be built up from base molecules in three ways:

$$-CH_2-CCl=CH-CH_2-CH_2-CCl=CH-CH_2-CH_2-CCl=CH-CH_2- \qquad (1)$$
$$-CH_2-CCl=CH-CH_2-CH_2-CH=CCl-CH_2-CH_2-CCl=CH-CH_2- \qquad (2)$$
$$-CH_2-CCl-CH_2-CH-CH_2-CCl-$$

$$\overset{|}{CH}=CH_2 \quad \overset{|}{CCl}=CH_2 \quad \overset{|}{CH}=CH_2 \qquad\qquad\qquad (3)$$

According to structure (1), succinic semialdehyde and succinic acid should be formed; according to structure (2) succinic dialdehyde and succinic chloroanhydride, and according to structure (3) considerable quantities of formaldehyde and a high-molecular polycarboxylic acid.

Since an almost quantitative yield of succinic acid is actually obtained, structure (3) must be rejected. The absence of succinic dialdehyde favors structure (1) rather than structure (2), although this is not conclusive evidence, since succinic dialdehyde and succinic chloroanhydride are very unstable under the conditions employed, i. e., an aqueous medium and the presence of hydrochloric acid, for decomposing the polychloroprene ozonide. We are therefore engaged at present in developing a method whereby these reactive compounds will remain unchanged.

The present work is confined to the determination, as nearly quantitatively as possible, of the base molecules of the individual polymers of chloroprene. Almost all the polymers yielded, as the chief decomposition product of their ozonides, succinic acid in yields around 80 to 95 per cent of the theoretical, according to the procedure followed.

EXPERIMENTAL PART

Determination of the Base Molecule of α-Polychloroprene

The ozonization method involves preparation of the ozonides, their decomposition, and a study of the decomposition products. Of the numerous methods for the decomposition of the ozonides, that method was chosen which gave yields of decomposition products most nearly approaching the theoretical. This made it possible to obtain conclusive evidence with regard to the base molecule of the particular polymer being studied.

At first the ozonide was decomposed by water alone, but this gave only a small

yield of succinic acid and 30 to 40 per cent of resin, with which nothing could be done. Accordingly resort was had to methods which gave higher yields, and the following methods already proposed for the decomposition of ozonides were utilized:

(1) Decomposition in the presence of an aqueous suspension of calcium carbonate;[1]

(2) Decomposition by anhydrous methyl alcohol containing about 3 per cent of hydrogen chloride;

(3) Decomposition by concentrated aqueous sodium hydrogen sulfite;[5]

(4) Decomposition by aqueous hydrogen peroxide;

(5) Decomposition by catalytic hydrogenation;[6]

(6) Ozonization in the presence of water in order to bring about the immediate decomposition of the ozonide.

The conditions under which the rubber was prepared, the method of ozonization, and the method of preparation of the reaction products are described in the following sections.

α-Polymer

Pure α-polymer was obtained by polymerization of 10–20 per cent pure polyprene, under which conditions it is the only polymer formed, as was proved in numerous experiments. The α-polymer of chloroprene is precipitated from its solution by dilution with petroleum ether (free of unsaturated compounds), and is purified by repeated solution in chloroform and reprecipitation by petroleum ether.

μ-Polymer is obtained by complete polymerization of chloroprene. In order to be certain of the result, the reaction mixture was let stand, with a little air space above it, for a long time (almost two months) in a tightly closed glass bottle. After removal of any α-polymer which might be present, the mass was finely divided, and was extracted in an atmosphere of nitrogen in a Soxhlet with chloroform until the solution no longer became turbid when alcohol was added.

Pure ω-polymer was obtained by inoculation of chloroprene with a little ω-polymer already prepared. To obtain ω-polymer completely free of μ-polymer, polymerization was carried out at only 10 to 15 per cent concentration. To remove α-polymer, the ω-polymer was extracted thoroughly with fresh portions of chloroform, and the solvent distilled off until the weight of product remained constant. In all these operations air was excluded as much as possible, since ω-polymer would otherwise resinify to a considerable extent.

To avoid decomposition, the α-polymer was not dried at first, but was dissolved directly in carbon tetrachloride or chloroform. The rubber content was determined by evaporation of an aliquot part of the solution in a vacuum and weighing of the residue.

Ozonization of the 15 to 10 per cent solution was carried out with 3–6 per cent ozone at a rate of 3–5 cm. per second, at −10° to −15° C., i. e., by cooling by means of a salt-ice mixture.

With carbon tetrachloride as solvent, the ozonide separated as a white gelatinous mass, whereas with chloroform it remained in solution.

In the first experiments, completion of the ozonization was ascertained by the bromine reaction in chloroform solution. In later experiments, however, it was proved that the bromination test is not reliable, because addition of bromine to the double bonds of the chloroprene polymer is not complete. Accordingly as a control in later experiments, a sample was treated with alcohol, and ozonization was continued until there was no longer any turbidity, since the ozonides are soluble in alcohol. In contrast, to the otherwise conventional method of Harries,[1] the ozonides were not separated by distillation to constant weight because they are unstable,

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and during the evaporation of the solvent they decompose with liberation of hydrogen chloride, even in a vacuum at room temperature. In some experiments, small quantities, *e. g.*, 0.05 gram, of crystals were found after distillation of the carbon tetrachloride. After washing with ether on a clay plate, these crystals fused at 116° C., and after recrystallization from hot water they fused at 180–181° C.; when mixed with pure succinic acid they fused at 180–181° C. These crystals as first obtained from the reaction product were probably succinic anhydride, which fuses at 120° C.

Decomposition of the Ozonides by Water

Three experiments on the decomposition of the ozonides by water were carried out. In these experiments approximately 25 per cent of succinic acid and 30 per cent of resin (based on the carbon skeleton) were obtained.

Ozonization of the rubber was carried out in carbon tetrachloride solution, with cooling by a mixture of ice and salt. In each experiment, 13.85 grams of rubber were used, and the ozonide was decomposed by heating with water for 9 hours. The resin formed was removed by filtration, dried to constant weight, and weighed. The water was distilled off in a vacuum, and the volatile acids in the distillate were determined by titration.

The quantity of volatile organic acids was determined from the difference between the total acid number and the amount of hydrochloric acid found by the Volhard method. The volatile acids were calculated as formic acid, which was determined qualitatively by mercuric chloride. Succinic acid, which remained in the residue of the distillation, was dried to constant weight and weighed. It fused at 180–181° C. The aqueous solution contained in addition a small quantity of aldehydes, which were identified in a few cases with dimethone.

Only with this reagent was there any precipitate, with melting point, before recrystallization, of 186° C. (a mixture with the condensation product of pure formaldehyde and dimethone fused at 187.5° C.). Condensation products with *p*-nitrophenylhydrazine, semicarbazide hydrochloride, and other reagents for aldehydes did not precipitate. Accordingly attention was confined in this experiment and in subsequent experiments to the titration of the aldehyde with hydroxylamine hydrochloride in the presence of bromophenol blue, and calculation as formaldehyde.

The results of the decomposition of the ozonides in two parallel series of experiments is described in the following paragraphs.

	Experiment I		Experiment II	
	Grams	Percentage[a]	Grams	Percentage[a]
Succinic acid	4.92	26.75	3.9	24.26
Volatile acids calculated as formic acid	0.5	1.7	0.35	1.04
Carbon dioxide combined with alkali	0.5	1.8	..	...
Carbon dioxide evolved during decomposition of the ozonide	0.5	1.8	..	...
Aldehydes calculated as formaldehyde	0.32	1.7	0.31	1.42
	..	33.75		26.72
Resin of unknown composition	4.00	28.88	5.5	34.22

[a] The percentage values are based on the carbon skeleton of the rubber subjected to ozonization.

The sum of the products of known structures is therefore 26.72 and 33.75 per cent of the carbon skeleton of the rubber subjected to ozonization. The total amount of all products was approximately 61 and 62.63 per cent, based on the rubber carbon skeleton.

To isolate the aldehydes and to prevent their resinification by hydrochloric acid, decomposition of the ozonide was carried out, in the presence of calcium carbonate. The attempt was also made to convert the aldehydes into more stable derivatives by carrying out the ozonide decomposition in the presence of sodium bisulfite or alcohol, so that acetal would be formed. The experiments in the presence of calcium carbonate were not successful, since a small yield of succinic acid was the only product. Resinification was also diminished but little. Resins were also formed in considerable quantities during decomposition of the ozonide chloroform solution by methyl alcohol containing 3 per cent of hydrogen chloride. This decomposition ran its course in 3 days at room temperature. The solution was neutralized with calcined potassium carbonate and then distilled in a vacuum. A small amount of a substance with boiling point of 48–55° C. (at 10 mm.) was isolated. This solidified in the freezing mixture and showed an ester number of 756 (calculated value of dimethyl succinate 768).

The second fraction, with boiling point of 100–140° C. (at 10 mm.), was a mixture of compounds which could not be studied further because of the small quantities. As residue from the distillation, a mobile, transparent oil was obtained, which also distilled under a pressure of 10 mm. of mercury without decomposition.

Decomposition of a cold chloroform solution of the ozonide with sodium bisulfite solution was also unsuccessful, because the reaction was too slow. Decomposition of the ozonide by concentrated sodium bisulfite solution in the absence of a solvent did not lead to the desired increased yield of ozonide decomposition products.

Ozonization of rubber was carried out in carbon tetrachloride in this experiment and in the succeeding one, for under these conditions the ozonide is precipitated; there is no solvent to remove by distillation, for it can be decanted, and thus danger of explosions is avoided.

The ozonide was then decomposed by agitation with concentrated bisulfite solution for 5 days. In one sample, no aldehydes were detected (negative reaction with fuchsin-sulfurous acid) even after 2 hours' warming with sodium bicarbonate and extraction with ether. This indicated either that no aldehydes were present or that the ozonide had not been decomposed. Accordingly in order to assure decomposition, the ozonide was warmed in the same bisulfite solution for 6 hours at 50° C. Under these conditions the solution became quite colorless, and a small amount of a light yellow oil settled to the bottom. Treatment of the solution with sodium bicarbonate dissolved the oil and colored the solution yellow. For final decomposition of the bisulfite compounds, the solution was kept warm for 5 hours; this caused considerable resinification and made the solution dark in color. The water was then distilled off in a vacuum. The distillate gave a negative aldehyde reaction, and the only product recovered was succinic acid.

Decomposition of the ozonide by hydrogen peroxide gave better results. The yield of decomposition products varied between 72 and 84 per cent of the weight of rubber. A yield of 70 to 80 per cent (based on the weight of rubber) of succinic acid was obtained as the chief decomposition product of the α-polymer ozonide.

Decomposition of the ozonide by concentrated hydrogen peroxide was carried out by warming for 5 hours on a water bath. Excess hydrogen peroxide was then decomposed by heating with platinum black, a reaction which proceeded rather slowly. The water was then distilled off in a vacuum, and the volatile acids in the distillate were determined and calculated as formic acid, the presence of which had previously been detected qualitatively. The residue yielded succinic acid.

Ozonide Decomposition Products	Grams	Yields Percentage
Succinic acid	9.15	82.3
Formic acid	0.38	2.2
Carbon dioxide	0.046	0.3
		84.8

The total yield represents 84.8 per cent of the carbon skeleton of the rubber subjected to ozonization.

Determination of the Base Molecule of the ω-Polymer of Chloroprene

In distinction to the α-polymer of chloroprene, the ω-polymer yielded an ozonide which was decomposed by water without any resinification. This accounts for the high yields, viz., 87 to 90 per cent, of succinic acid.

The ω-polymer was obtained by polymerization of chloroprene by means of inoculation, and was purified in the usual way.

A weight of 13.5 grams of substance was ozonized by treatment for 122 hours with 3 per cent ozone at the rate of 3 cc. per second, cooling with an ice-salt mixture. The ω-polymer was suspended in chloroform, and during ozonization it gradually passed into solution. Ultimately 0.4 gram of a white substance was precipitated, which fused at 170° C., with considerable resinification. This was probably composed of crystals of succinic acid, which had been formed by partial decomposition of the ozonide.

The chloroform was distilled from the ozonide in a vacuum at 20° C., under which conditions frothing took place, evidently from incipient decomposition.

The ozonide was decomposed by water by warming for 4 hours, whereby it dissolved completely. When water was added to the ozonide which had been dried to constant weight, a considerable rise in temperature took place, and the ozonide passed into solution with a loud hissing sound.

To isolate the decomposition products of this ozonide, the water was removed by distillation in a vacuum. This left as a residue pure succinic acid, which after recrystallization fused at 180–182° C. The succinic acid was dried to constant weight and determined by titration. Aldehydes were determined by titration with hydroxylamine in the presence of bromophenol blue. They were not identified more exactly because precipitates could not be obtained with the usual reagents.

The yields were as follows:

Product	Grams	Percentage
Succinic acid	15.35	85.25
Formic acid	0.92	3.30
Formaldehyde	0.25	1.35
		89.90

The sum of the decomposition products amounted to 89.90 per cent of the carbon skeleton of the polymer. An experiment on the decomposition of the ozonide of the ω-polymer by a 10 per cent solution of hydrogen peroxide was carried out. The preparation of ω-polymer and its ozonization were the same as in the preceding experiments. The yield of ozonide from 19 grams of polymer was 25.95 grams, i. e., an 87.2 per cent yield. Forty minutes after addition of the hydrogen peroxide the temperature increased markedly, the liquid reached the boiling point, and all ozonide passed into solution. To moderate the reaction, 50 cc. of distilled water were added. This precipitated a crystalline substance which fused at 183–184° C. The aldehyde reaction with fuchsin-sulfurous acid was negative.

The yields were as follows:

Product	Weight	Percentage
Succinic acid	22.4	87.1
Formic acid	0.12	0.3
		87.4

Determination of the Base Molecule in μ-Polymer

The μ-polymer of chloroprene formed, as did the ω-polymer, an ozonide which, in distinction to that of α-polymer, was decomposed by water without resinification and with a good yield of succinic acid.

μ-Polymer was prepared by polymerization of chloroprene in an atmosphere of nitrogen for a period of 2 months. It was a transparent mass, which was cut into small pieces and extracted in a Soxhlet apparatus after swelling in chloroform. The μ-polymer was then dried to constant weight in a vacuum and again suspended in chloroform. Ozonization of 5 grams was carried out with 3–4 cc. of ozonized oxygen per second for 45 hours, with cooling by ice. When all powder had passed into solution, the chloroform was removed from the ozonide by distillation.

The ozonide was decomposed by heating in water for 5 hours, under which conditions the ozonide completely dissolved. The decomposition products were isolated by distilling off the water; this left a yellowish residue of succinic acid, with melting point of 179–181° C. The aldehydes were determined by titration with hydroxylamine, using bromophenol blue as indicator.

The following yields were obtained by this decomposition:

Product	Grams	Percentage
Succinic acid	4.81	72.15
Formic acid	0.37	3.5
Formaldehyde	0.24	3.5

This represented a total yield of 79.15 per cent of the carbon skeleton of the μ-polymer which was ozonized. The same result was obtained in an attempt to ozonize 58.5 grams of μ-polymer in the presence of water, so that the decomposition of the ozonide would take place during ozonization.

The succinic acid thus obtained fused at 181–183° C. The water distillate contained 5.75 grams acid calculated as formic acid. The aldehyde reactions were negative. The yields were as follows:

Product	Grams	Percentage
Succinic acid	58.19	81.57
Formic acid	5.75	5.2

This gave a total of 86.77 per cent, based on the carbon skeleton of the rubber.

It was proved in these experiments that the base molecules of the three types of polyprenes, viz., the α-, μ-, and ω-polymers, are built up of chains of four carbon atoms, since succinic acid was the chief product of the decomposition of the ozonide with all three polymers. The question of the aldehydes and their nature, as well as the question of the splitting of the ozonides by some method which gives higher yields of the aldehydes, will be treated in a later communication.

In addition to the experiments with ozone, an attempt was made to oxidize the α-polymer of chloroprene by nitric acid. The rubber was treated with concentrated nitric acid (density 1.40) on a boiling water bath until the rubber was completely decomposed. The following decomposition products were obtained as a result of this treatment.

(1) Succinic acid.
(2) Oxalic acid.

(3) A yellow, amorphous substance, which gave brown solutions in aqueous alkalies.

(4) A viscous oil, which was not studied further.

A control experiment showed that, when oxidized by nitric acid, succinic acid yields oxalic acid. It is noteworthy that in the oxidation of natural rubber by nitric acid, Harries obtained products of analogous compositions.

These oxidation reactions therefore confirm the ozonization reactions.

Résumé

(1) The ozonization of the α-, μ-, and ω-polymers of chloroprene, including ozonization in the presence of water, and the subsequent decomposition of the products by water, hydrogen peroxide, and sodium bisulfite were studied.

(2) The best results in the decomposition of ozonides of the α-polymer were obtained with hydrogen peroxide.

(3) In the case of the μ-polymer, the best results were obtained by ozonization in the presence of water.

(4) Succinic acid was the chief product of ozonization, and this fact gave conclusive evidence regarding the nature of the base molecule of polychloroprene.

(5) In the oxidation of α-polyprene by nitric acid, succinic acid and oxalic were found among the products.

(6) The structure of polychloroprene is shown in detail.

The decomposition of the ozonides of the polychloroprenes by hydrogenation will be described in a forthcoming publication.

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The Amorphous and Crystalline Forms of Rubber Hydrocarbon

George S. Park

CORRECTION

The article commencing on page 135 of the January 1937 issue of this Journal should have the title above, i. e., the word "Amorphous" is spelled incorrectly in the January issue. The error also appears in the table of contents of the January issue.
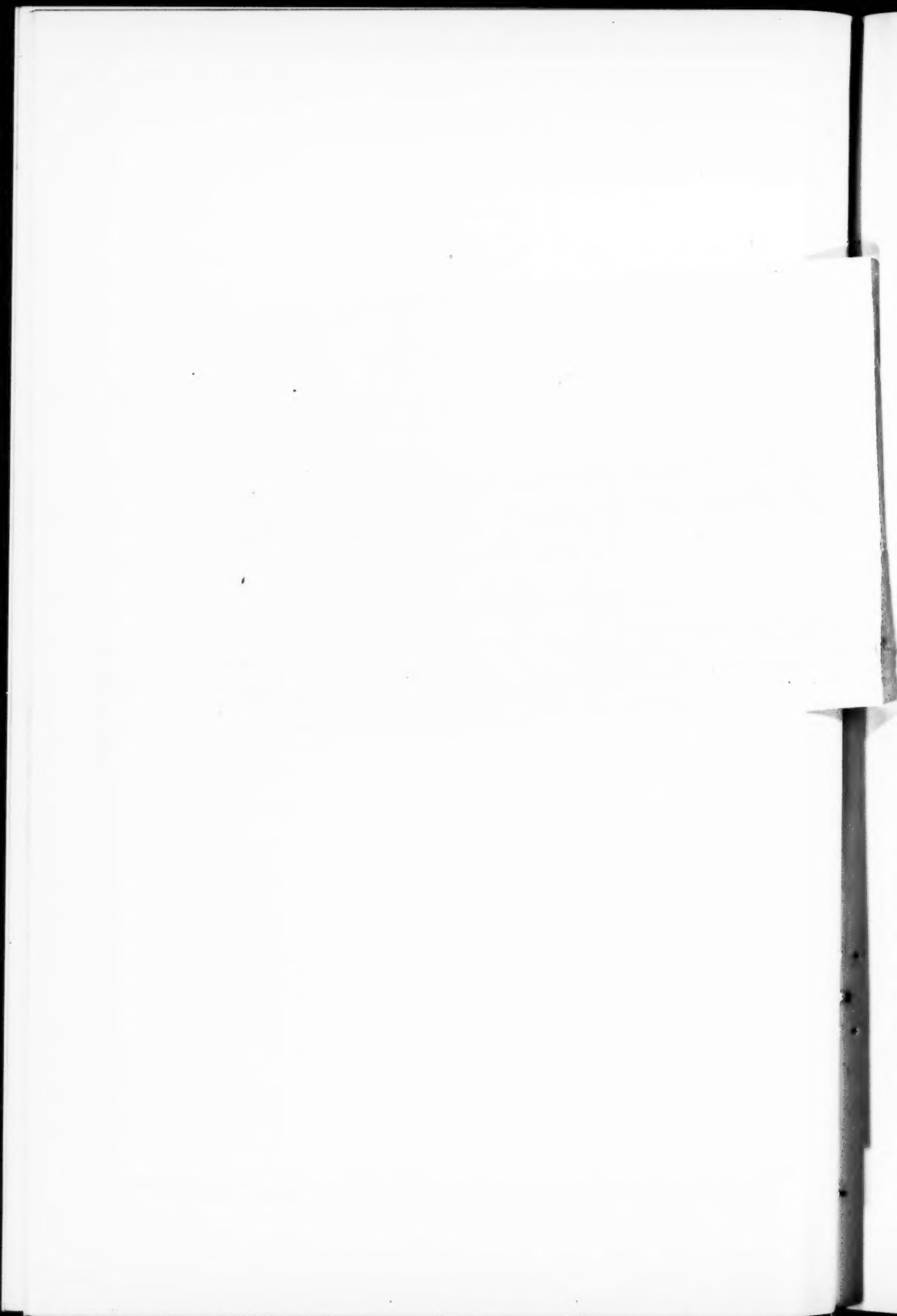
The Amphorous and Crystalline Forms of Rubber Hydrocarbon

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The coefficients of thermal expansion and the heat capacities of rubber hydrocarbon, both in an amorphous and in a so-called crystalline form, have been recently reported in two papers by Bekkedahl and Matheson.[1] According to these investigators, the amorphous form undergoes a transition of the second order in the neighborhood of 199° K. Above this temperature they found a rather abrupt increase of approximately 205 per cent in the volume coefficient of thermal expansion, and one of about 38 per cent in the heat capacity. These phenomena are strikingly similar to those found in numerous studies on glasses in this laboratory, and especially in the recent investigation on polyisobutylene by Ferry and Parks.[2] Thus, with the particular sample of polymerized isobutene employed, the *transition region* centered around 197° K. and the subsequent increases in volume coefficient and heat capacity were 200 and 32 per cent, respectively.

Bekkedahl and Matheson found that, by cooling the amorphous rubber hydrocarbon to about 230° K. and then permitting it to warm up slowly over a period of days, their material could be obtained in a "crystalline" form. These "crystals" melted at 284° K. with a heat of fusion of 4.0 calories per gram. They also exhibited the previously mentioned second-order transition at about 199° K., but with somewhat smaller subsequent increases with rising temperature, *i. e.*, about 165 per cent increase in the volume coefficient of thermal expansion and 28 per cent in the heat capacity. Two facts appear surprising and highly significant with these "crystals": (1) the value of the heat of fusion which is extremely low compared with the figures of 20 to 54 calories per gram hitherto reported for various aliphatic hydrocarbons melting near room temperature,[3] and (2) the duplication of the second-order transition found previously for amorphous rubber hydrocarbon.

The writer of this communication feels that these two facts can best be explained by the supposition that Bekkedahl's "crystals" really represent a mixture of amorphous and crystalline rubber hydrocarbon. Assuming that the second-order transition is due solely to the amorphous hydrocarbon, he estimates the percentage of this in the so-called crystals to be about 80 from the relative increases of the volume coefficients above 199° K. Similarly from the relative increases of the heat capacities above this transition, he estimates 71 per cent amorphous material in the "crystals." These estimates check only roughly, but in this connection it is important to note that the two types of measurements were made upon different samples, and that the sample used for the specific heat measurements was contaminated wth 2.8 per cent oxygen. The presence of such a large percentage of amorphous substance in this "crystalline" form is not really surprising in view of the high molecular weight of rubber hydrocarbon, and the probability that the material contains a variety of molecules representing various degrees of polymerization of C_5H_8. In fact, similar but not such extensive contamination of the crystalline form with amorphous material has previously been observed in this laboratory with such relatively simple substances as ethyl alcohol, *n*-amyl alcohol,[4] and lactic acid.[5] In the case of the last named, Parks, Thomas, and Light, on

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crystallizing the liquid, obtained a two-phase system with about 12 per cent amorphous material.

On the basis of his hypothesis of 71 per cent amorphous material in the rubber hydrocarbon crystals of Bekkedahl and Matheson, the writer has obtained from their data an estimate of 17.4 calories per gram for the heat of fusion of pure crystals. This estimate is of the same order of magnitude as the values reported previously for many other paraffin and olefin hydrocarbons melting above 200° K.

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[1] Bekkedahl, *Bur. Standards J. Research*, **13, 411** (1934); Bekkedahl and Matheson, *Ibid.*, **15, 503** (1935).

[2] Ferry and Parks, *J. Chem. Phys.*, **4,** 70 (1936).

[3] See, for example, Parks and Huffman, *Ind. Eng. Chem.*, **23,** 1138 (1931).

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Gutta-Percha

Effect of Vulcanization on Its X-Ray Diagram

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EARLY x-ray investigations by Clark (2) and Ott (13) on gutta-percha and balata established the fact that these materials were crystalline in nature even in the unstretched condition. In 1927 Hauser and his co-workers (5) pointed out the similarity of the diagrams obtained on gutta-percha and balata, but it remained for Hopff and Susich (7) to establish definitely the identity of the x-ray diagrams of the two substances. In addition they brought out the interesting fact that, on heating above 60° C., a characteristic change took place in the gutta-percha diagram. Hauser and Susich (6) made a detailed study of this change. They showed that gutta-percha (and hence also balata) underwent a change in crystalline structure at about 68° C. The beta modification, obtained above this temperature, did not transform back into the low-temperature or alpha form, but remained unchanged unless the cooling took place very slowly through the transition point. The last-named authors gave much attention to the securing of well-oriented fiber patterns of both crystalline forms in order to calculate their respective identity periods along the fiber axis. Their results, which are probably the most reliable published to date, give the alpha form of the hydrocarbon an identity period of 8.78 ± 0.12 Å. and the beta form an identity period of 4.87 ± 0.07 Å. More recently Bruni and Natta (1) have examined gutta-percha by means of electron rays and have given a solution for the alpha[1] form in which they find the unit cells to be orthorhombic and to have the axes: $a = 6.53$ A., $b = 7.68$ Å., and $c = 9.60$ or 4.80 Å. (fiber period). They find the number of isoprene units (C_5H_8) per cell to be four.

The present work relates to the investigation of vulcanized gutta-percha hydrocarbon by means of x-rays. No record of such a study has been found in the literature, although it

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[1] Bruni and Natta (1) list their data as applying to the alpha form of gutta-percha but employ the identity period of 9.60 which corresponds not to the alpha but to the beta modification. Since these authors find the alpha spacing 3.3 Å., it is probable that their samples contained both modifications. In view of the fact that the layer-line reflections cannot be indexed when the identity period given by Hauser and Susich for alpha gutta-percha is employed, it seems improbable that the unit cell of Bruni and Natta can be correct for alpha gutta-percha. In addition, in the present work it is shown that this unit cell does not agree with the x-ray data for beta gutta-percha.

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is well known that vulcanization of gutta-percha with sulfur
leads under certain conditions of cure to a material possessing
distinct rubber-like properties when warmed (*14*). Preliminary
tests on samples of gutta-percha vulcanized for various times
showed that after "melting"—i. e. heating until translucent—
the samples remained amorphous for a time which increased
with the time of cure. Samples previously melted and
exposed to x-rays in the stretched condition at room tempera-
ture showed the orientation characteristic of the cold drawn
samples but lost their reversible stretch during the time of
exposure. However, the fiber patterns of the stretched vul-
canized samples showed a considerably higher degree of
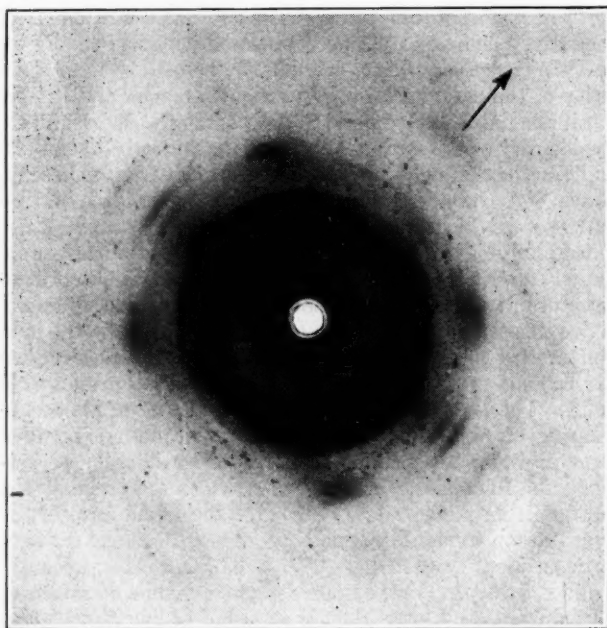
FIGURE 1.   FIBER DIAGRAM OF GUTTA-PERCHA CONTAINING
SULFUR AND ACCELERATOR BUT NOT VULCANIZED
Reflections are due to uncombined sulfur; film distance, 39.6 mm. Arrow
indicates direction of stretch.

orientation than was generally obtained by stretching gutta-
percha alone. Therefore, these fiber diagrams were studied
in the light of the work on gutta-percha and balata just sum-
marized with the hope that more information on the crystal
structure of these hydrocarbons might be obtained.

X-Ray Technic

The source of the x-rays was a Philips' Metalix x-ray tube with
a copper target ($\lambda = 1.539$ Å.).   The tube was operated at ap-
proximately 25 kilovolts and passed a current of 15 milliamperes.
A nickel filter 0.015 mm. in thickness was employed to absorb
the K beta radiation of copper.   The wave length corresponding

to the maximum intensity of the continuous x-ray spectrum was evident on certain photographs but, it is believed, in no case led to an erroneous measurement.

The cameras employed were similar to those described by Katz (8). The distance of the sample from the photographic film was varied between 3 and 5.5 cm. and was checked by two methods: (a) a Debye-Scherrer photograph of a bar of finely powdered sodium chloride crystals and (b) accurately measured stops which could be inserted between the sample holder and the film support. When corrections were made for the thickness of the sample of sodium chloride and for the thickness of the black paper covering the film, the two methods checked to 0.02 mm. Holders of brass were provided for the samples so that they
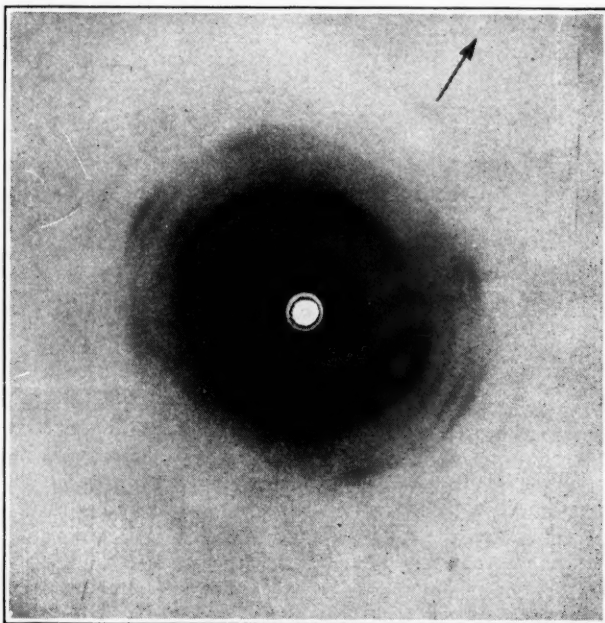
FIGURE 2. MIXED FIBER DIAGRAM OF ALPHA AND BETA GUTTA-PERCHA, NOT VULCANIZED

Film distance, 39.6 mm.

could be maintained in a condition of maximum stretch during the exposure. The time of exposure in most cases was 6 hours.

Measurements on the photographs were made to the nearest 0.1 mm., a precision which was sufficient in view of the size of the reflections obtained. This precision, on separate check photographs at different plate distances, was approximately 1 per cent of the distance being measured and in many cases was less than 0.5 per cent of this distance. The percentage error for measurements of the same photograph was less than 0.5 per cent except in rare cases.

Preparation of Samples

Two grades of gutta-percha were employed: (a) a pure white Tjipetir hydrocarbon containing 0.05 per cent p-tolui-

dine as antioxidant (this material was obtained in vacuum tins direct from the Dutch Government Tjipetir Plantation), and (b) a fourth-grade gutta-percha with a somewhat higher resin content (1 per cent) and 0.05 per cent hydroquinone. Vulcanized samples were prepared from both grades and had the composition: gutta-percha, 94 per cent; sulfur, 5; zinc butyl xanthate (accelerator), 1. These samples were cured at 142° C. for times ranging from 15 minutes to 3.5 hours. A set of control samples was also prepared from each of the grades of gutta-percha. They contained the hydrocarbon, sulfur and accelerator in the proportions
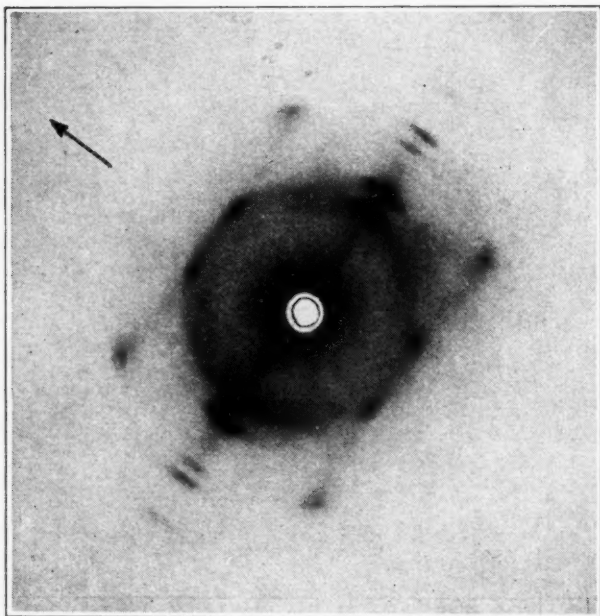
FIGURE 3. FIBER DIAGRAM OF BETA GUTTA-PERCHA VULCANIZED FOR ONE HOUR AT 142° C.
Film distance, 44.3 mm.

given, but were not subjected to cure. X-ray photographs of these latter samples showed reflections due to the uncombined sulfur crystals superimposed on the gutta pattern, but otherwise were the same as those of the uncompounded gutta-perchas. This effect is shown in Figure 1.

A few photographs were also taken of samples of deresinated balata (containing approximately 1 per cent resin) prepared from the latex of *Mimusops Gaertn.* These verify the finding that the x-ray diagrams of balata and gutta-percha are identical. The results are given in the last column of Table I.

For the purpose of taking the x-ray diagrams, the samples

were cut into strips about 1 mm. wide and 1.3 mm. thick. Except in the case of samples which were oriented by drawing cold, the procedure was to warm the strip by immersing it in water at 80° C. for several minutes and to stretch immediately on removal from the bath to the maximum degree possible without breakage. The tension was maintained until

TABLE I. COMPARISON OF LATTICE PLANE SPACINGS OF SAMPLES OF VULCANIZED AND UNVULCANIZED GUTTA-PERCHA, IN ÅNGSTRÖM UNITS

Reflection[a]	1[b]	2[c]	3[d]	4[e]	5[f]	6[g]	7[h]	8[i]
$A_2\ \alpha$	7.92	..	7.97	..	7.87	..	..	7.85
$A_3\ \beta$ or α	..	..	6.90	..	6.80	6.75	..	..
$A_4\ \beta$	5.97	..	5.94	..	5.92	5.94	..	5.92
$A_6\ \alpha$	..	..	5.01	..	..	4.93	..	4.99
$A_7\ \beta$	4.71	4.73	4.71	4.70	4.75	4.75	4.75	4.73
$A_8\ \alpha$	3.92	3.90	3.91	3.89	3.91	3.91	3.92	3.93
$A_9\ \alpha$	3.35	..	3.31	..	3.32	3.33	3.30	3.33
$A_{11}\beta$	3.00	2.95	3.00	2.95	3.00	2.98	2.99	2.94
$A_{12}\beta$	2.80	2.75	2.80	2.74	2.79	2.78	2.78	2.74
$A_{13}\beta$	2.38	2.36	2.37	2.36	2.38	2.38	2.37	2.35
$A_{14}\alpha$ or β	..	..	2.12	..	2.12	..	..	..
$A_{16}\beta$	1.98	..	1.95	1.93	1.96	1.95	..	1.93
$II_1\ \beta$	..	..	4.44	..	4.45	4.46	..	4.44
$II_2\ \beta$	..	..	3.90	..	3.84	3.88	..	..
$II_3\ \beta$	..	..	3.50	..	3.48	3.51	..	..
$II_4\ \beta$	..	..	3.12	..	3.14	3.14	..	..
$II_5\ \beta$	2.95	2.91	2.92	2.94	2.95	2.94	..	2.93
$II_6\ \beta$	..	..	..	..	2.42	2.43	..	..
$II_7\ \beta$	..	..	..	..	2.25	2.25	..	..
$I_1\ \alpha$	..	..	5.08	..	5.13	5.05	..	5.07
$I_2\ \alpha$	..	..	4.55	..	4.55	4.52	..	4.58
$I_3\ \alpha$	..	..	4.05	..	4.04	4.05	..	4.06
$I_4\ \alpha$	..	..	3.32	..	3.32	3.33	..	3.32
$I_5\ \alpha$	..	..	2.72	..	2.72	..	..	2.69
$II_1\ \alpha$	..	..	3.50	..	3.48	3.48	..	3.50

[a] In assigning symbols to the equatorial reflections, the alpha and beta reflections have been grouped in the same scheme in descending magnitude of their spacings.
[b] Pure Tjipetir gutta-percha hydrocarbon.
[c] Fourth-grade gutta-percha (1 per cent resin).
[d] Sample 1 containing the ingredients for vulcanization.
[e] Sample 1 vulcanized 15 minutes at 142° C. (vulcanization coefficient 1.65).
[f] Sample 1 vulcanized 30 minutes at 142° C. (vulcanization coefficient 1.96).
[g] Samples 1 and 2 vulcanized 60 minutes at 142° C.
[h] Sample 1 vulcanized 210 minutes at 142° C.
[i] Deresinated balata from *Mimusops Gaertn* latex.

cool (25° C.). This operation was repeated three times. The elongation so produced was about 500 per cent for the vulcanized and about 1500 per cent for the unvulcanized samples. The samples were exposed in the state of maximum extension by means of the holders mentioned previously.

Results

A comparison of the lattice plane spacings of the various samples of gutta-percha described leads to the conclusion that the presence of the vulcanization ingredients either in the uncombined or combined state has no detectable effect on the gutta-percha spacings. This appears to be equally true of both forms of the crystals and for all of the vulcanized samples independent of their time of vulcanization. Table I, which summarizes these spacings for a number of samples including both alpha and beta forms, illustrates this point. Since the measurement of the lattice plane spacings can be

made with equal accuracy whether a high degree of orientation is attained or not, the agreement is taken as evidence that the crystal structure of gutta-percha was unchanged by the vulcanization to which it was subjected in these experiments.

As illustrated in Figures 2, 3, and 4, however, vulcanization with sulfur has an effect in increasing the degree of orientation produced by stretching. Figure 2 shows the effect of stretching gutta-percha (not vulcanized) after warming to 80° C. as described. Figures 3 and 4 show the effect of stretching the same gutta-percha according to the same procedure except that in these cases the gutta-percha had been previously
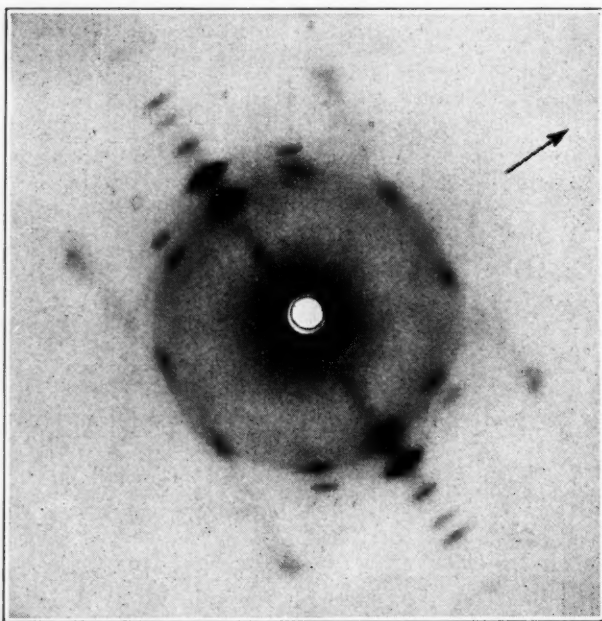
FIGURE 4. MIXED FIBER DIAGRAM CONTAINING BOTH THE ALPHA AND BETA FORMS OF GUTTA-PERCHA OBTAINED FROM GUTTA-PERCHA VULCANIZED FOR ONE HOUR AT 142° C.

Film distance, 55.6 mm.

vulcanized for one hour at 142° C. As might be expected from the reduction in plastic flow caused by vulcanization, the vulcanized samples show a much higher degree of orientation than do the unvulcanized. Furthermore, a comparison of the fiber diagrams obtained on samples vulcanized one-half to one hour with those of unvulcanized samples oriented by cold drawing showed that a higher degree of orientation was obtained in the case of the vulcanized samples.

These diagrams show further that, although the same

sample of vulcanized gutta-percha was employed in the case
of both Figures 3 and 4, the former is an almost pure diagram
of the beta modification whereas the latter shows the presence
of a mixture of the alpha and beta forms. Hence under the
conditions of stretching employed here, the transition alpha
to beta does not always appear to be irreversible. On the
basis of previous work (6) a beta diagram would be ex-
pected since in all cases the gutta-percha was heated to 80° C.
prior to stretching.

In view of the high degree of orientation obtained in the
fiber patterns of vulcanized gutta-percha, accurate measure-
ments of the identity periods of both forms were possible.
Several of the photographs showed the presence of almost
pure beta gutta-percha as indicated by the absence of the
equatorial reflection A_9. The average lattice plane spacings
and identity periods for these are given in Table II with data
of Hauser and Susich, Bruni and Natta, and Stillwell and
Clark (16) for comparison. In general, the agreement is
good so that the value of the identity period for this form may
be considered to be very close to 4.80 Å. or some multiple of
this figure.

TABLE II. AVERAGE VALUES OF LATTICE PLANE SPACINGS
AND IDENTITY PERIODS OF BETA GUTTA-PERCHA COMPARED
WITH PREVIOUS WORK, IN ÅNGSTRÖM UNITS

Reflection	Present Work		Hauser and Susich[a]		Bruni and Natta		Stillwell and Clark
	d	IP	d	IP	d	IP	d
?A_1[b]	9.35	..	..	..	..	..	..
A_3[b]	6.75	..	..	..	..	..	..
A_4	5.95	..	..	..	..	..	..
?A_5	5.22	..	..	..	..	..	..
A_7	4.73	..	4.8	..	..	..	4.73
A_8	3.91	..	3.9	..	3.86	..	3.89
A_{10}[b]	3.15	..	..	..	..	..	..
A_{11}	2.98	..	..	..	..	..	2.95
A_{12}	2.78	..	..	..	..	..	2.77
A_{13}	2.37	..	..	..	2.48	..	..
A_{14}[b]	2.12	..	..	..	..	..	..
A_{15}	2.02	..	..	..	..	..	..
A_{16}	1.95	..	..	..	1.90	..	..
II$_1$	4.45	4.79	4.56	4.91	..	..	..
II$_2$	3.87	4.78	3.88	4.94	..	..	..
II$_3$	3.51	4.80	..	..	..	..	..
II$_4$	3.08	4.75	3.17	4.83	..	..	..
II$_5$	2.93	4.79	2.89	4.79	2.95	..	..
II$_6$	2.42	4.78	..	..	..	..	..
II$_7$	2.25	4.76	..	..	2.22	..	..
IV$_0$ (diatrope)	2.36	4.72	..	..	2.42	..	..
IV$_1$	2.02	4.74	..	..	2.04	..	..

Average identity period (c axis):
Present work   4.77 ± 0.03
Hauser and Susich   4.87 ± 0.07
Bruni and Natta   4.80

[a] The lattice plane spacings for the layer-line points were calculated from
data given by these authors (6, p. 149).
[b] It is uncertain whether these reflections belong to the alpha or the beta
diagram.

First an attempt was made to fit the observed reflections
into the scheme proposed by Bruni and Natta (1). It was
found, however, that suitable indices could not be assigned
to the reflections A_4, A_5, A_7, A_{12}, II$_1$, II$_4$, II$_6$ on this basis.
Consequently the method of Sauter (15) for the evaluation

of fiber diagrams was applied to the reflections listed in Table II. In this way it was found possible to account satisfactorily for all of the observed reflections including those of Bruni and Natta. The dimensions of the unit cell for beta gutta-percha by this method resulted as follows: $a = 15.7$ or 7.85 Å., $b = 11.9$ Å., $c = 4.77$ or 9.54 Å. (fiber period). An ortho-rhombic cell is indicated. Figure 5 illustrates the relation of these unit cells to one another.

It is difficult to choose between these various unit cells on the basis of the observed x-ray spacings alone. However, the larger spacing for the a axis is favored by the presence of the reflection II_3 and by the fact that it agrees better with one of the reflections observed by Bruni and Natta (2.48 Å.).

TABLE III. COMPARISON OF OBSERVED AND CALCULATED LATTICE PLANE SPACINGS FOR BETA GUTTA-PERCHA[a]

Reflection	hkl	$d_{calcd.}$ (Å.)	$d_{obsvd.}$ (Å.)	Relative Intensity[b]
?A_1[c]	110	9.48	9.35	VW
A_3[c]	210	6.55	6.75	VW
A_4	020	5.95	5.95	VW
?A_6	300	5.23	5.22	VW
A_7	310	4.78	4.73	VVS
	220	4.73		
A_8	400	3.92	3.91	VS
	320	3.93		
A_{10}[c]	330	3.15	3.15	VW
A_{11}	040	2.97	2.98	M
	510	3.03		
A_{12}	240	2.78	2.78	S
	430	2.79		
A_{13}	440	2.37	2.37	S
	050	2.38		
	620	2.39		
	150	2.35		
A_{14}[c]	720	2.10	2.12	VW
	540	2.16		
A_{15}	450	2.03	2.02	VW
	060	1.98		
A_{16}	640	1.96	1.95	M
	800	1.96		
II_1	012	4.43	4.45	M
II_2	212	3.86	3.87	W
II_3	302	3.52	3.51	VW
II_4	032	3.05	3.08	W
II_5	412	2.93	2.93	M
II_6	242	2.40	2.42	W
	432	2.41		
II_7	612	2.25	2.25	W
	342	2.27		
IV_0	004	2.37	2.36	W
IV_1	414	2.01	2.02	W

[a] $a = 15.7$ Å.; $b = 11.9$ Å.; $c = 9.54$ Å.; $\beta = 90°$.
[b] V = very; W = weak; S = strong; M = moderate.
[c] It is uncertain whether these reflections belong to the alpha or the beta diagram.

Likewise there is no x-ray evidence which allows a definite choice between the values 4.77 and 9.54 for the fiber period, since the accepted chain molecule structure for gutta-percha may possess a glide plane of symmetry parallel to the chain axis. The larger unit cell of Figure 5 was chosen here as the basis for index assignment because it allows all of the data listed in Table II to be included. Assuming a density

(*10*) of 0.982 for crystalline gutta-percha, we obtain 15.4 (approximately 16) isoprene groups as the number occupying this unit cell. This unit cell has a volume approximately four times that found by Bruni and Natta since the *a* and *b* axes are each about twice those found by these investigators.

Table III gives the indices found for each point by means of the graphical analysis, the comparison of the observed and calculated lattice plane spacings, and the relative intensities of the observed reflections for a cell of these dimensions. The following formula has been used for the calculation of the lattice plane spacings:

$$\frac{1}{d^2} = h^2 (0.00407) + k^2 (0.00706) + l^2 (0.0110)$$

No fiber diagrams in which it was certain that the alpha form of gutta-percha was present alone were obtained. For

TABLE IV. AVERAGE VALUES OF LATTICE PLANE SPACINGS AND IDENTITY PERIODS OF ALPHA GUTTA-PERCHA COMPARED WITH PREVIOUS WORK, IN ÅNGSTRÖM UNITS

Reflection	Present Work		Hauser and Susich[a]		Bruni and Natta
	d	IP	d	IP	d
A_2	7.91	..	7.7	..	..
A_6	4.95	..	4.9	..	..
A_8	3.91	..	3.9	..	3.86
A_9	3.33	..	3.3	..	3.28
I_1	5.08	9.04	4.78	8.76	..
I_2	4.54	8.94	4.52	8.85	..
I_3	4.05	8.78	4.02	8.80	..
I_4	3.32	9.02	3.29	8.76	..
I_5	2.72	8.55	2.69	8.68	..
II_1	3.49	9.04	3.48	8.74	..
III_1	2.64	8.77	..	..	..

Average identity period (*c* axis):
Present work   9.00 ± 0.05
     8.70 ± 0.13
Hauser and Susich   8.78 ± 0.12

[a] The lattice plane spacings for the layer-line points were calculated from data given by these authors (*6*, p. 149).

this reason no attempt has been made at a complete treatment of this modification. The measurements of the reflections, however, indicate certain peculiarities that have not been observed heretofore. Table IV gives the average lattice plane spacings and identity periods along the fiber axis calculated for the reflections not included in the beta diagram, together with those of Hauser and Susich (*6*) and Bruni and Natta (*1*) for comparison. Table IV shows that the identity periods calculated for the various layer-line reflections do not agree well with each other or with the data of Hauser and Susich. Since the deviations appear to be greater than the experimental error of measurement, it is difficult to regard all of the reflections as arising from the same crystalline form. Attempts to apply the graphical method to the solution of this fiber pattern employing an average value for the identity period failed to account satisfactorily for all of the observed reflections. It is rather surprising, however, that all of the equatorial reflections except A_6 are readily indexed by the scheme found to apply to the beta diagram.

Discussion

The influence of sulfur in producing better orientation of the crystallites in gutta-percha is interesting in the light of the theories of rubber vulcanization. Apparently no parallel exists in rubber in which case vulcanization appears to require stretching to greater elongations in order to produce the fiber pattern (*2, 9*). In the case of sol rubber, however, Clark and co-workers (*4*) have recently found that vulcanization causes the appearance of a fiber pattern at 400 per cent elongation whereas elongations of 1000 per cent do not cause crystallization without vulcanization. In the case of gutta-percha the increased orientation produced by vulcanization seems to be connected with the reduction in plastic flow of the vul-
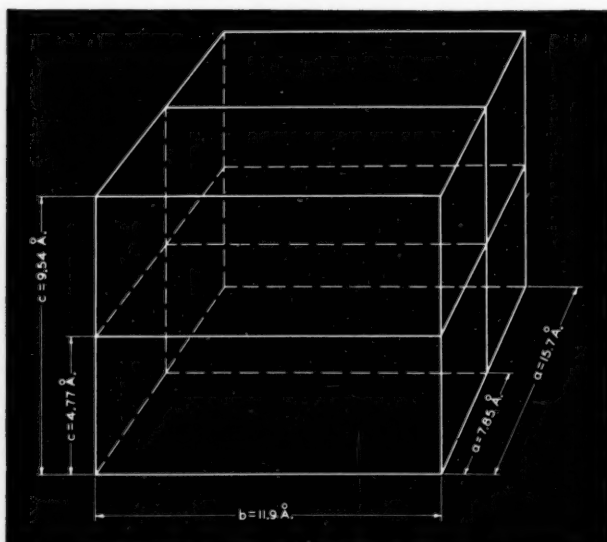

FIGURE 5.   POSSIBLE UNIT CELLS FOR BETA GUTTA-PERCHA

canized material at the temperatures employed to produce the orientation (80° C.). Hence the orientation effect can be interpreted as being due to the fact that the chain molecules in the vulcanized samples are restrained from flowing from the positions of parallelism which they assume as a consequence of the stretching force. This could well be effected by the hooking together of shorter molecules by sulfur bridges so as to form longer ones which many believe occurs in the vulcanization of rubber.

The observation (Figure 4) that both the alpha and the beta forms of gutta-percha may crystallize out together when a sample of the vulcanized hydrocarbon is cooled from 80° C. and at the same time is subjected to a stretching force, finds an interesting explanation by Hauser and Susich (*6*). These

authors state that, on cooling gutta-percha from temperatures above the transition point (68° C.), the alpha form does not crystallize out at its freezing point (65° C.) because of its low crystallization velocity, and that from the supercooled melt at temperatures below the freezing point of the beta modification (56° C.), only the latter form is then capable of crystallizing. In the present instance we evidently have an example in which the rate of crystallization of the alpha modification has been greatly accelerated by the application of the stretching force so that a considerable portion is caused to crystallize in the interval 65° to 56° C. Since this effect was not observed in the unvulcanized samples, it is possible that the presence of sulfur also plays a part in favoring this crystallization.
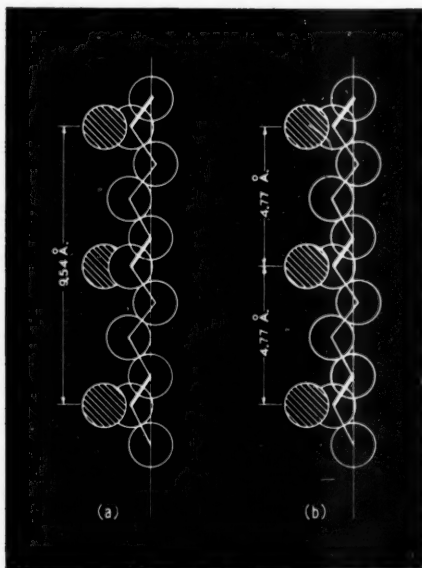
FIGURE 6. TWO TYPES OF THE GUTTA-PERCHA CHAIN

(a) Repeating distance, 9.54 Å.
(b) Repeating distance, 4.77 Å.

The finding of the repeating distance 4.77 Å. along the fiber direction in beta gutta-percha agrees well with the calculated length (4.80 Å.) of the *trans* form of the gutta-percha chain as has been pointed out by Meyer and Mark (*12*). This fact makes it probable that the chain molecules of gutta-percha are extended with their long axes parallel to the *c* axis of the unit cell—that is, parallel to the direction of stretch. Such an arrangement of the molecules is in agreement with the structures proposed for other high-molecular substances such as cellulose and rubber.

If the length, 4.77 Å., is the true identity period in the fiber direction, it is necessary that the methyl groups lie on the same side of the plane which includes the chain carbon atoms. If, on the other hand, the true identity period in this direction is 9.54 Å. as has been assumed above, the methyl groups will lie on opposite sides of this plane. These two possibilities are shown in Figure 6. As stated before, present evidence does not permit a choice between these two fiber periods. Since, however, the presence of one of the types of chains of Figure 6 is well supported by both the chemical and x-ray evidence, it is probable on the basis of the symmetry possessed by these chains that the beta gutta-percha crystals belong to the crystal class C_{2v} of the ortho-rhombic system. This conclusion follows from the fact that the other two crystal classes of this sytesm—namely, V_h and V—both require three mutually perpendicular twofold axes of symmetry, a condition which is difficult to satisfy with structures of the type represented in Figure 6.

Just as it is possible for the unit cell of beta gutta-percha to have a c axis one-half that assumed in Table III, so by neglecting the reflections indicated as questionable or uncertain in Table II we can arrive at a unit cell having an a axis one-half as great. Thus, assuming that the reflections A_1, A_5, A_{10}, A_{14}, and II_3 (the latter is weak and difficult to measure) do not belong to the beta diagram, the remaining h indices of column 2, Table III, become divisible by 2 and therefore allow an a axis one-half as large. The base of this unit cell will measure 7.85×11.9 Å. and will have space for four chain molecules to pass perpendicularly through it. It is interesting to note the nearness of these dimensions to those (8.3×12.3 Å.) proposed for the base of the unit cell of stretched rubber by Susich (*12*). However, it is not likely that beta gutta-percha will conform to as high a class of symmetry as does rubber to which Meyer and Mark have attributed the crystal class V or V_h.

Until the dimensions of the unit cell for beta gutta-percha are established definitely, there is little purpose in attempting to determine its space group and ultimately the atomic positions in the crystal. For until these dimensions are known, it is not possible to distinguish between the presence of simple planes and glide planes of reflection or between simple axes and screw axes of symmetry, and it is thus difficult if not impossible to arrive at the correct space group. Richer fiber diagrams of this form of gutta-percha or the production of specimens in which a higher order of orientation is achieved will aid in this determination. But as has been often pointed out (*8*, *11*), in the absence of suitable macroscopic crystals it will be necessary to employ all available chemical and physical evidence in order to arrive at a convincing solution of this phase of the crystal structure.

No attempt at a complete treatment of the alpha diagram of gutta-percha is possible on the basis of the evidence ob-

tained so far. It is difficult to explain the discrepancies that apparently exist in the identity period calculated for this diagram. Rather than attribute a very long identity period to the gutta-percha molecule [Clark (3) reported finding such spacings in rubber and cellulose], it seems more reasonable to postulate the existence of three forms of the hydrocarbon with fiber periods 4.77, 9.00, and 8.70 Å. or multiples of these figures. The latter two are represented by the points of Table IV. Speculations of this nature, however, are of little value until further data are secured. One result of this work has been to show that the crystal structure of gutta-percha is considerably more complicated than generally has been realized. Only by continued investigation by means of x-rays and electron rays can the true solution of the crystal structure of this and other high-polymeric substances ultimately be solved. It is hoped that the experiments summarized here will serve as a step in the direction to this solution.

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Natural and Synthetic Rubber. XVI. The Structure of Polystyrene

Thomas Midgley, Jr., Albert L. Henne and Henry M. Leicester

Polystyrene[1] is a friable solid which exhibits rubber-like properties at temperatures above 65°; it is obtained by heat polymerization of styrene.

Staudinger and his co-workers[2] have stated that polystyrene can be decomposed by heat into a mono-, di-, and tristyrene; that the latter two compounds can be decomposed to monostyrene; and that 2,4-diphenyl-1-butene and 1,3-diphenylpropane can be detected among the heat decomposition products. They have therefore reached the conclusion that polystyrene is a long chain of styrene units bound together by ordinary valences, with a phenyl group linked to every second carbon. They have advocated formula I and rejected formula II.

$$—CH_2CHPhCH_2CHPhCH_2CHPh— \tag{I}$$
$$—CH_2CHPhCHPhCH_2CH_2CHPhCHPhCH_2— \tag{II}$$

Staudinger's experiments were repeated and found to be correct but the following additional facts were noted: (1) heat decomposition of polystyrene does not yield monostyrene exclusively; (2) rapid decomposition yields large amounts of monostyrene, while slow decomposition yields "di-styrene," "tri-styrene," and other intermediate products; (3) the partially decomposed products are complicated mixtures, and their further decomposition gives a poor yield of monostyrene; (4) diphenylbutene and diphenylpropane are present in very small quantities, and only on products obtained from incomplete decomposition; (5) all efforts to analyze the dimeric fraction by oxidation, reduction, nitration, bromination, etc., gave indifferent results. These additional experimental data cast strong doubts on the significance of the decomposition products in establishing the formula of polystyrene.

An explanation of dependence of the elasticity of natural and synthetic rubbers on their structural formula has been offered by Mack.[3] The application of his ideas to the case of polystyrene leads directly to the conclusion that the elastic properties of this substance are consistent with formula II, and not at all with the heretofore accepted formula I, for the following reasons.

In the case of formula I, the 1,3-placement of the phenyl groups results in optimum packing of the phenyl groups, optimum contacting of the hydrogen atoms, and good satisfaction of the van der Waals forces *when the chain molecule is extended;* consequently there is no tendency to fold or shorten the chain. But in the case of formula II, the 1,4-placement throws the phenyl groups together into pairs on adjacent carbon atoms, with two chain carbon atoms separating these pairs. Not only do the two phenyl groups within a pair turn into one another to establish better contacting, but van der Waals forces draw together into contact the various separate pairs, thus folding the extended chain and giving automatic retraction, hence elastic, rubber-like behavior. The motion of the bulky phenyl groups is sluggish at room temperature, but becomes freeer and swifter with increasing thermal agitation, *i. e.,* at higher temperature.

Since Staudinger's reasons for discriminating against the formula required by

Mack's theory were not found convincing, it was decided to apply to styrene the experimental procedure previously used with isoprene and dimethylbutadiene to establish the course of their transformation into synthetic rubber and methyl rubber, respectively.[4] This procedure consists in stopping the polymerization at the dimeric stage by addition of nascent hydrogen generated by the interaction of sodium and ethanol. Sodium chips are added to styrene and alcohol is fed at a rate sufficient to produce a lively evolution of hydrogen; the reaction liberates a considerable amount of heat, but the boiling of the alcohol automatically regulates the temperature. The reaction products consist of about 75% of ethylbenzene and 25% of 1,4-diphenylbutane. Significant is the fact that the reaction products are pure and entirely free from isomers or by-products.

The course of the polymerization is interpreted as follows. If the thermal agitation of the liquid styrene molecules consisted only of Dulong and Petit motions, back and forth, polymerization could take place by the random linking of two carbon atoms in α-position (with regard to the phenyl group), two carbon atoms in β-position, or one α- and one β-atom, and consequently the two phenyl groups of the dimeric compounds would be located in 1,4-, 2,4-, or 2,3-position. The molecules are, however, in a liquid, and therefore crowded; they are thus compelled to rotate about the center of their own volume, that is, close to the center of the phenyl group. Then, no matter how the rotation occurs, the β-carbon atoms, at the end of the side-chain, are the only ones which can eventually come close enough to link. The chances of an α-carbon coming close enough to a β-carbon of another molecule to link are very remote, and its chances of coming close enough to another α-carbon are nil, because in addition to being shielded by the bulky phenyl group, it is most effectively buried within the sphere of revolution established by the outlying CH_2 group. As soon as two molecules have linked together the dimeric compound assumes a shape such as:[5]
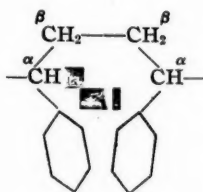
where the free bonds of the α-carbon atoms are now at the surface and ready to join with the bonds of another dimer. From this stage the process of polymerization takes place by mere repetition.

It is therefore concluded that formula II is the correct representation of polystyrene and that Mack's explanation of its elasticity is consistent with the facts. This conclusion has been obtained in private discussion with Dr. Mack, whom we wish to thank.

Experimental

Preparation of Diphenylbutane with Sodium and EtOH.—Alcohol was added dropwise to 17 g. (20 cc.) of freshly distilled styrene and 5.3 g. of sodium chips at such a rate that hydrogen was steadily evolved. During the first part of the reaction, it was necessary to cool the mixture occasionally. As the reaction proceeded the solution became brown and sodium alcoholate separated, so that when all the sodium had been used up, the reaction mixture was almost solid. Ether was then added and the solution washed three times with water and dried over calcium chloride. The

combined ether extracts from three runs (totaling 62 g. of styrene) were fractionated. Two fractions were obtained, one boiling at 135–150°, the other at 304–308°. The latter solidified in the receiver. The first fraction weighed 46 g. (74%) and consisted of ethylbenzene containing almost no styrene, as shown by the facts that no polymerization occurred when sulfuric acid was added to the liquid, or when it was heated for a prolonged period of time. The solid material, which weighed 11.5 g. (18.5%) after crystallization from alcohol, melted sharply at 52–52.5°, and the melting point showed no depression when the crystals were mixed with 1,4-diphenyl-butane prepared by the catalytic reduction of 1,4-diphenylbutadiene.[6] The mother liquors from the crystallization were diluted with water and extracted with ether. From the extract was obtained 2 g. (4.3%) of a semi-solid yellow oil from which more 1,4-diphenylbutane separated.

Summary

Styrene treated with sodium and alcohol gives 75% of ethylbenzene and 25% of 1,4-diphenylbutane. This shows that polystyrene should be represented by formula II, in opposition to the heretofore accepted formula I. Only formula II is consistent with Mack's explanation of the rubber-like elastic properties of polystyrene.

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Studies of Hard Rubber Reactions

III.   Changes in the Acetone Extract during Vulcanization

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In the former communications (Part I and Part II) the author dealt with the characteristic changes in some physical properties with time of cure of hard rubber compounds.   The work has now been extended by chemical observations.   In the first place, the author studied the acetone extract of the same compounds of the previous reports with a view to ascertaining the nature of the hard rubber reactions.

Preliminary Examination of the Acetone Extract

Samples were prepared for acetone extraction in two ways.   In the case of soft rubber products, the material was sheeted out to thin crepe by passing between the tightly closed rolls of a laboratory mill and was then cut with scissors into fine strips. Hard rubber samples were prepared by buffing with an alundum grinder and sifting through a 100-mesh screen.   In each case the sample taken for the extraction was 0.5–1.0 gram.

The extraction apparatus was a new design, as illustrated in Fig. 1, which has the advantage of extracting the sample in the vapor of boiling acetone, and in many other respects is more efficient and convenient than the Cottle type of extractor.

There has been considerable discussion as to a standard time of extraction for hard rubber.   According to the specification of the Society of Rubber Industry of Japan, for example, extraction of at least 48 hours is recommended, while it is specified in the British Standard Specification No. 234 (1933) that only 8 hours of continuous extraction are necessary for ebonite for electrical purposes.   Besides these, extraction periods of 72 hours, 20 hours, etc., have been advocated by various authors.

Preliminary tests were carried out with the extractor mentioned above, with a mixture of rubber 100, tetramethylthiuram monosulfide 2, zinc oxide 10, stearic acid 1; vulcanized for 30 and 120 minutes at 141° C.

The results are shown in Table I.

Considerable difficulty was experienced, as in experiments on the extraction of free sulfur by Stevens and Stevens (*J. Soc. Chem. Ind.*, **48**, 55T (1929)), in removing the entire free sulfur, and also acetone-soluble organic matter, even for a longer period of 150 hours' extraction.   An extremely long extraction does not mean the elimination of the true acetone-soluble substances, but suggests that secondary chemical changes, such as depolymerization of hard rubber products, may occur.

The second tests were carried out with mixtures of rubber 100, sulfur 5, 25, 50, 100, 150, diphenylguanidine 2, zinc oxide 10, stearic acid 1; vulcanized for 60, 180, and 300 minutes at 141° C.   The conclusions of the experiments may be summarized as follows:

(1)   In the case of hard rubber samples, 75–85 per cent (mean value of 81.0 per cent) of the total acetone extract which was obtained by 50 hours' extraction, were extractable within 12 hours, and about 85–95 per cent (mean value of 92.5 per cent) within 20 hours.

TABLE I

	Minutes of Cure	Hours of Extraction								
		5	10	20	30	40	60	80	100	150
Acetone Extract Less	30	1.84	2.77	2.78	2.79	2.94	2.98	3.08	3.77	4.15
Free Sulfur (%)	120	3.29	3.33	3.57	3.68	3.72	3.79	3.94	4.12	4.83
Free Sulfur (%)	30	9.24	9.35	9.46	9.47	9.47	9.58	9.60	9.66	9.70
	120	0.84	1.02	1.00	1.00	1.00	1.01	1.01	1.11	1.20

(2)   Though removal of free sulfur was nearly as complete after 20 hours as after 50 hours, it was impossible to reach the final point of extraction.

As complete acetone extraction was not attainable even after extremely long ex-
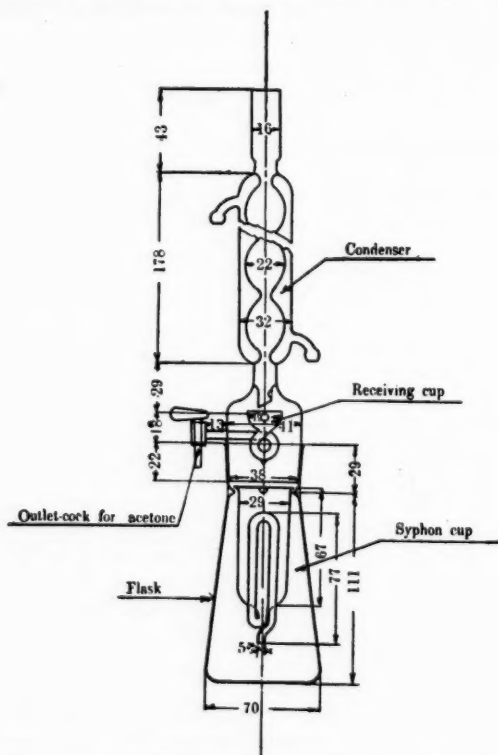
Figure 1—Acetone Extractor (All Dimensions in Mm.)

traction, comparisons in the present investigation were made on a basis of 20 hours as the most reasonable and convenient time of extraction.

Results of the Acetone Extraction

In general, as shown in Figs. 2 to 5, the amount of extract decreased gradually until the time of cure about 60 minutes was attained, probably because of polym-
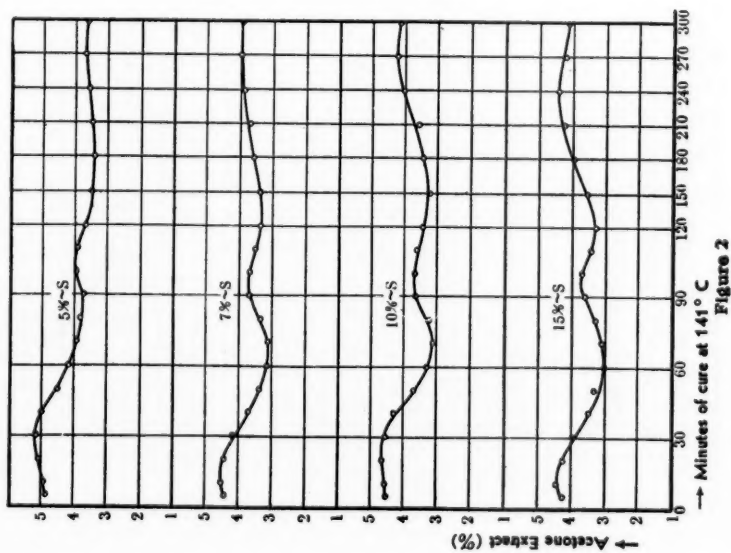
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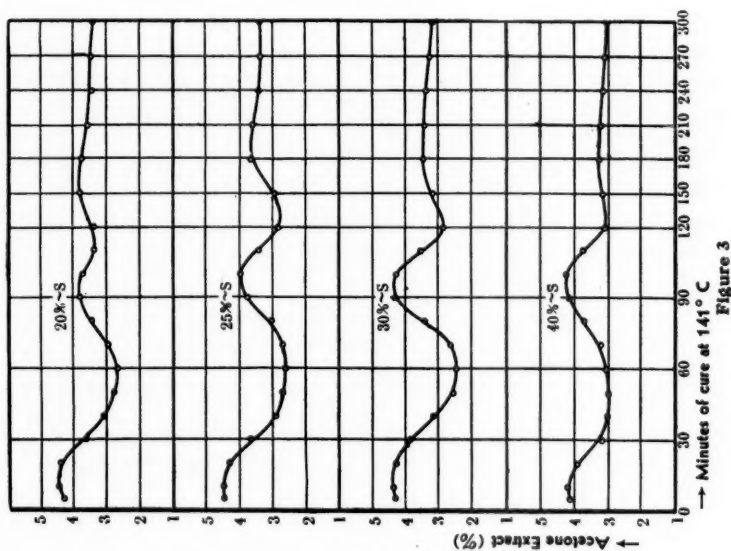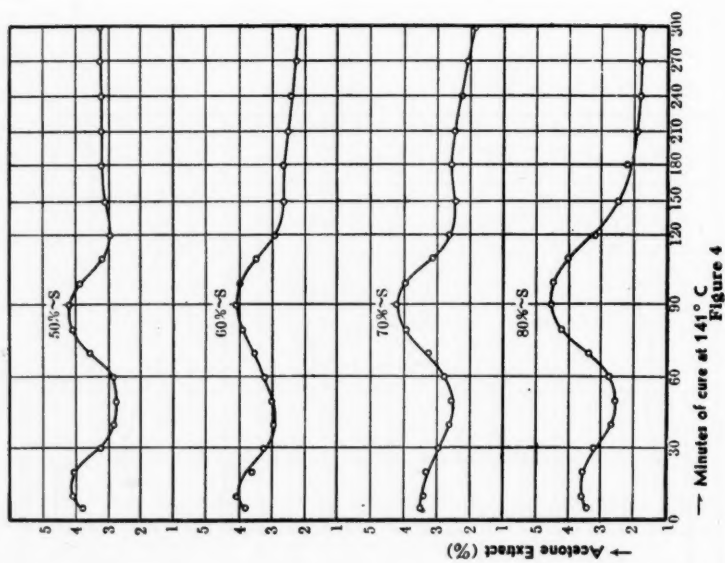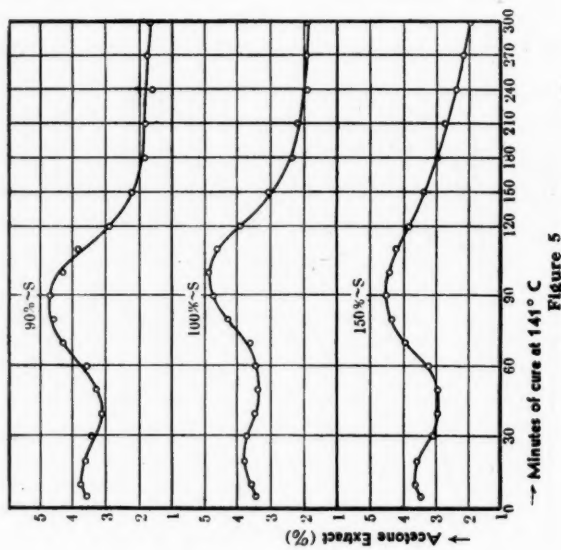
Figure 2

Figure 3

Figure 5

Figure 4

erization.   After about 90 minutes, all acetone extract curves showed intermediate maxima as did the elongation curves (cf. Part I).   The increase in the acetone extract with time of cure may be ascribed to the effect of heat.

In view of the facts above, polymerization and depolymerization of rubber or of vulcanized rubber products seem to take place simultaneously by the effect of heat.   The parallelism between the changes in acetone extract and some of the physical properties, such as tensile strength, elongation and hardness, indicates that at a definite time of about 90 minutes after the beginning of cure, the hard rubber reaction, accompanied by depolymerization may have taken place, with a subsequent rapid hardening or polymerization of the hard rubber products.

The Mode of Action of Disulfide Accelerators of Vulcanization

W. Langenbeck and H. C. Rhiem

· GREIFSWALD, GERMANY

The catalytic power of organic compounds in general has up to the present time been studied much less extensively than that of inorganic compounds. For about the last ten years, however, the first author has, in collaboration with a number of his students, attempted to fill this gap,[1] though so far efforts have been confined to explaining the mode of action of natural enzymes by means of comparative experiments with organic catalysts. As a result of this work, a theory based on experimental facts has been developed to explain in a satisfactory way the action of enzymes.

The other phase of organic catalysis is, strictly speaking, a technical problem. Why for instance should it not be practicable to utilize organic catalysts more extensively than heretofore in industry? If this problem is to be attacked, it seems reasonable to start with the particular industry which already uses organic catalysts to the greatest extent. This is, of course, the rubber industry. The important accomplishments of the chemical industry with respect to the development of vulcanization accelerators is already common knowledge, and the important task at present is not simply to increase the great number of accelerators already known. A problem of more practical value would seem to be to study the mechanism of the acceleration of vulcanization, about which relatively little has been known heretofore.

In a study of the mechanism of any catalytic reaction, the most important task is first to search for active intermediate compounds which may be formed. If it is possible to demonstrate the existence of compounds of accelerator and sulfur or of accelerator and rubber, it becomes highly probable that these substances play an active intermediary role during vulcanization. It has in fact been generally assumed that accelerators combine with sulfur, and since the work of Bedford and Scott[2] the accelerating action of organic bases has been attributed to the fact that in the presence of small quantities of hydrogen sulfide these bases form polysulfides with sulfur. In spite of this, however, the formation of sulfur compounds of the industrially most important accelerators, i. e., mercaptans and disulfides, has never been proved conclusively.

The present authors have confined their attention chiefly to disulfides, since they are more stable than mercaptans. To establish the existence of compounds of disulfides and sulfur, the obvious thing to do seemed to be to fuse the accelerators with sulfur alone, and then to attempt to isolate crystalline addition compounds from the fusion mixtures. A simple experiment showed, however, that this is as a general principle impossible.

In the first experiment the solubility of an ultra-accelerator, tetramethylthiuram disulfide, in pyridine in the presence of sulfur was determined, and it was found that the solubility of the two components together is approximately double the sum of the solubilities of the individual components.

SOLUBILITY (GRAMS PER CC.) IN PYRIDINE AT 25°

Experiment	Thiuram	Sulfur	Sum	Thiuram + Sulfur
I	0.0648	0.0153	0.0801	0.1636
II	0.0710	0.0135	0.0845	0.1683

In this solubility determination, the two substances (0.6 gram of tetramethyl-thiuram disulfide; 0.3 gram of sulfur) were agitated with 3 cc. of pyridine for 3 days in a thermostat at 25° C. (Experiment I).   To reach equilibrium from the direction of saturation as well, the two substances were first dissolved at approximately 50° C., and were then allowed to crystallize for 3 days in a thermostat at 25° C. (Experiment II).   The results of the two series are in approximate agreement.   Agitation for a longer time seemed inadvisable, since the solutions became gradually darker in color.

These experiments in themselves prove conclusively that tetramethylthiuram

Figure 1—Thaw-Fusion Diagram of the System: Naphthalene-Sulfur
O Melting Point
X Thawing Point
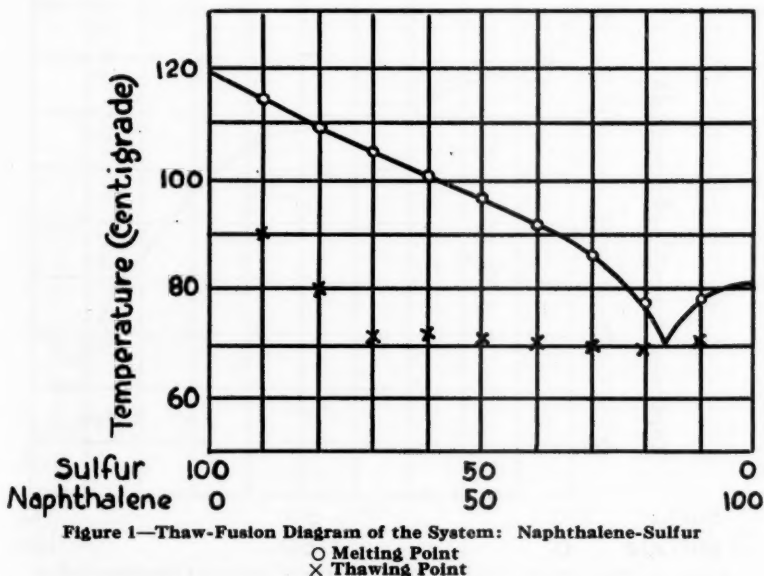
disulfide and sulfur form a compound. Since, however, this compound is more soluble than the components and also partially dissociates in solution, crystallization of the solution always yields only the unaltered components. In the same way an attempt to isolate a compound from a fusion mixture of benzothiazyl disulfide and sulfur by recrystallization from carbon disulfide yielded only pure benzothiazyl disulfide.

As an alternative means of establishing the existence of such addition compounds, which are too loosely bound to be isolated, the construction of a fusion diagram is useful. This method gives, moreover, an indication of the compositions of the new compounds, which obviously cannot be learned merely from solubility experiments. Rheinboldt has developed a useful method for organic substances. In this method various proportions of the two components are fused together, the fusion mixture is allowed to solidify and the behavior of the mixture in a melting point apparatus studied.

As the temperature increases, a small part of the mixture first melts. This temperature is called the "thawing point," and it corresponds to the melting point of the eutectic. The temperature at which the residual part melts is recorded on the diagrams as the "melting point."

In this way a fusion curve is obtained, which shows maxima at the points where compounds are formed. It will of course be understood that pure substances must be used, and that they must not decompose at the temperature of fusion. Benzothiazyl disulfide conforms to this last requirement, whereas tetramethylthiuram disulfide does not, so that with the latter compound an increase in solubility was the only evidence which could be obtained.

Since benzothiazoles contain aromatic rings, attention was first directed to
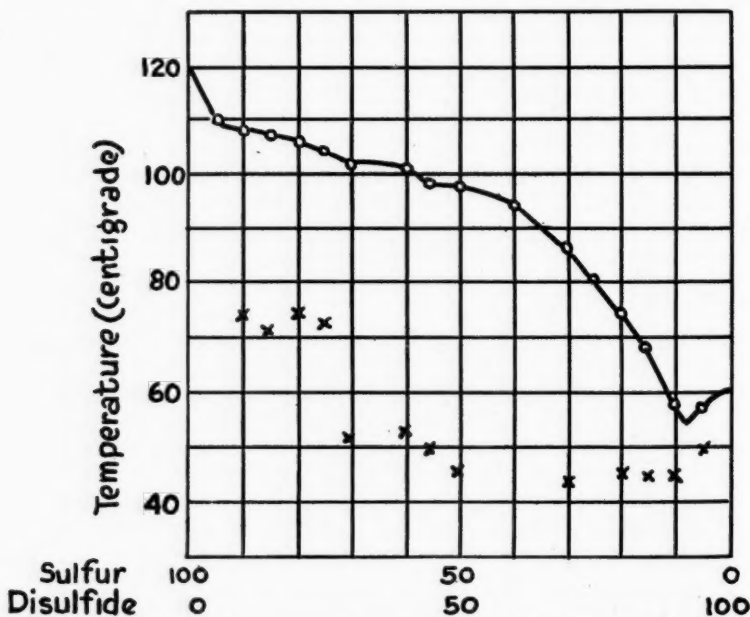
Figure 2—Thaw-Fusion Diagram of the System: Diphenyl Disulfide–Sulfur
O Melting Point
X Thawing Point

ascertaining whether aromatic hydrocarbons themselves form loosely bound compounds with sulfur. This is evidently so, for the system naphthalene–sulfur gave a normal fusion diagram without any maxima, as may be seen in Fig. 1. The thawing points lie predominantly on a straight line parallel to the abscissa, at the temperature of the eutectic point.

Quite otherwise is the general appearance of the fusion diagrams of the simplest aromatic disulfides. As typical examples of these, mixtures of diphenyl disulfide and of β-dinaphthyl disulfide with sulfur were studied. The results are shown in Figs. 2 and 3.

The curves show individual bends or deflections which are very flat, and show in some cases no maxima. This is the trend of a curve which contains concealed maxima, and which are always present when the compounds have a particularly

marked tendency to dissociate. The thawing points then give a characteristic curve with pronounced temperature breaks, as is especially evident in Fig 2. In any case these compounds which have absolutely no accelerating activity, form no stable addition compounds.

With the system: dinaphthyl disulfide–sulfur, and still more so with the systems to be described, a difficulty was encountered in that the fusion mixtures crystallized very slowly. In a few cases it was necessary to let the mixtures stand for several weeks at 50° C., and even then crystallization was frequently incomplete. In spite of this, the melting points were determined, because by waiting still longer there was the danger that part of the sulfur would volatilize. Because of this incomplete crystallization, the thawing points are in some cases too low. As a result the thawing curves do not always touch the eutectic points, as required by
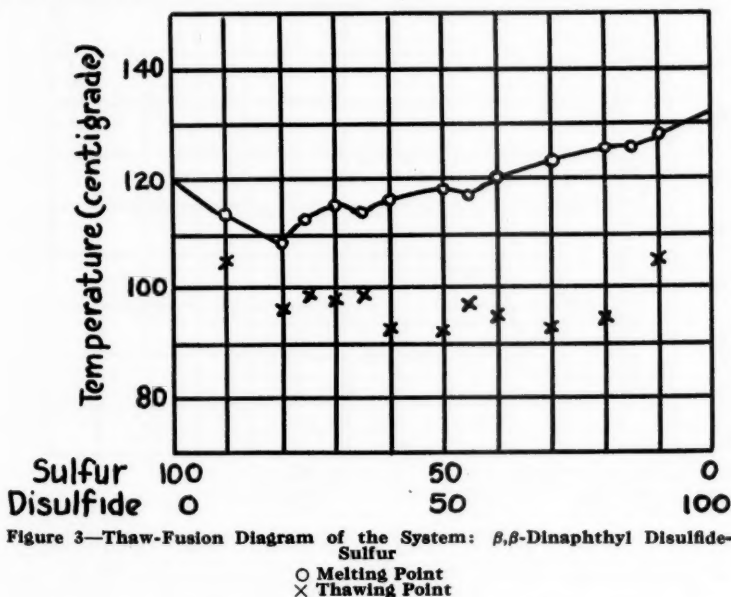
Figure 3—Thaw-Fusion Diagram of the System: β,β-Dinaphthyl Disulfide–Sulfur

O Melting Point
X Thawing Point

theory. Many fusion mixtures were far from being strictly solid, and therefore could not be measured.

Let us now examine the fusion diagrams of two representative semiultra-accelerators, benzothiazyl disulfide[3] and α-naphthothiazyl disulfide. It is evident at once that the maxima of these curves are much more sharply defined than those of the curves of the disulfides containing no nitrogen. Benzothiazyl disulfide gives three maxima, one of which certainly corresponds to a compound, disulfide S_2. The accuracy of the method does not make it possible to establish the composition of compounds richer in sulfur, but they contain from 20 to 25 and from 80 to 100 molecules, respectively, of sulfur per molecule of disulfide. The compound with approximately 20 molecules of sulfur is also evident in the case of naphthothiazyl disulfide. However, in this case a compound with a higher sulfur content is merely suggested by a slight bend in the curve.

What type of structure these substances rich in sulfur may possess is difficult to decide. At the moment it seems possible that macromolecules, which sulfur

is known to form readily,[4] are attached in a coördinate system to the organic disulfide. In any case these compounds belong to an entirely different type from the group of dibenzothiazyl polysulfides which were obtained from mercaptides and sulfur chloride by Levi,[5] and which have much lower melting points.

The conclusive evidence that accelerators form compounds with sulfur makes it highly probable that these compounds represent intermediate products in the acceleration of vulcanization. In favor of this idea is the fact that catalytically active disulfides show more sharply defined melting point maxima, i. e., give more stable addition compounds, than do inactive disulfides. Sulfur is activated to such an extent that it combines with the accelerator. On the other hand a contrary argument is the observation of Bruni and Romani[6] that tetramethylthiuram disul-
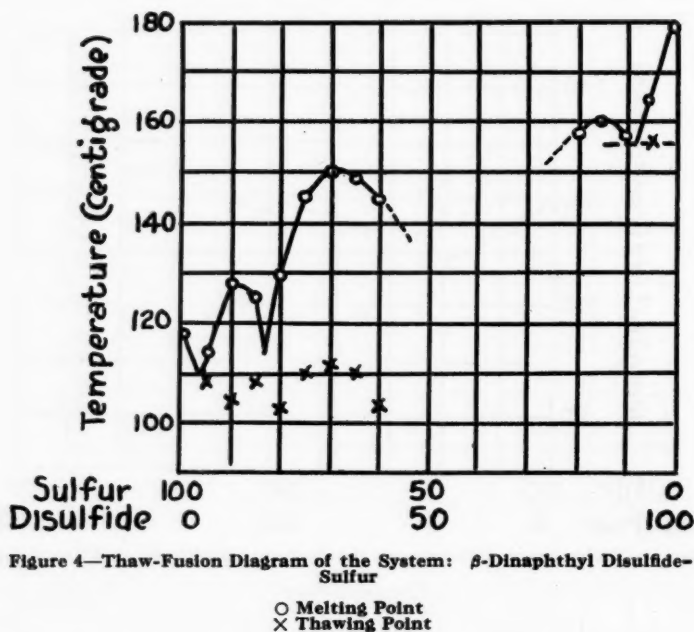
Figure 4—Thaw-Fusion Diagram of the System: β-Dinaphthyl Disulfide–Sulfur

O Melting Point
X Thawing Point

fide first liberates sulfur and then combines with it again. Furthermore Braun and Weissbach[7] have shown that on heating tetramethylthiuram disulfide, it decomposes irreversibly, with liberation of sulfur and formation of tetramethylthiourea, thus: $(CH_3)_2NC(:S)SSC(:S)N(Me)_2 \rightarrow [(CH_3)_2N]_2CS + CS_2 + S$. This reaction explains why tetramethylthiuram disulfide vulcanizes rubber, even in the absence of sulfur. In this case sulfur is liberated in an active form. However, a catalytic action is out of the question, in fact vulcanization can be accomplished with tetramethylthiuram disulfide at temperatures much below its temperature of decomposition, viz., approximately 140° C.

Finally a study was made of the influence of zinc oxide, without which sulfides have no accelerating power. It is natural to assume in this case the formation of a complex between accelerator and zinc oxide. The existence of a complex of this character in the case of mercaptobenzothiazole is already established, for Spacu and Kuras[8] have recently shown that the zinc derivative is not a simple

mercaptide, but a complex of the composition: $(C_7H_4NS_2)_3Zn_2OH$. In all probability it has an internal complex structure, and it may be considered to be the basic zinc salt of a zinc mercapto acid, thus: In the present work it was not found
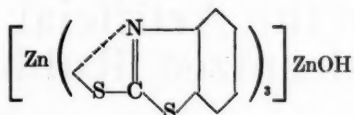
possible to isolate any corresponding complex compounds of disulfides. Nevertheless it was found that benzothiazyl disulfide was somewhat soluble in hot concentrated zinc chloride solution, but wholly insoluble in water. It may therefore be
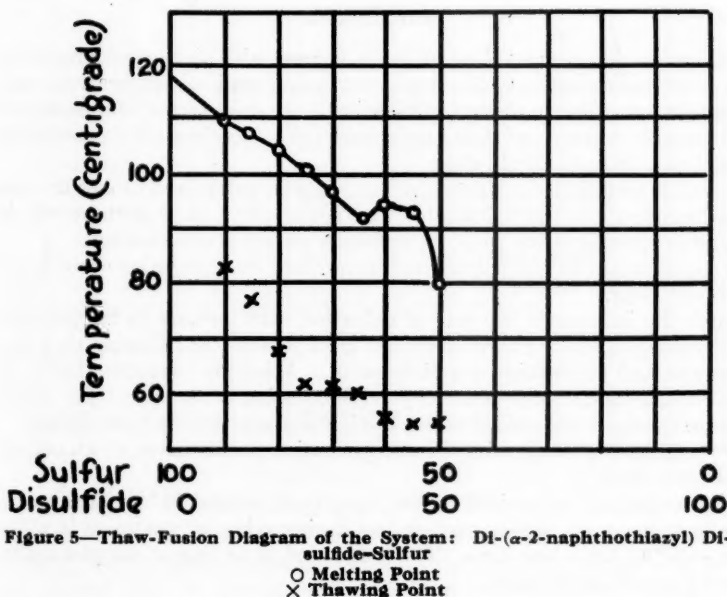
Figure 5—Thaw-Fusion Diagram of the System: Di-(α-2-naphthothiazyl) Disulfide–Sulfur

O Melting Point
X Thawing Point

assumed provisionally that the activity of accelerators is increased by the formation of complex derivatives with zinc oxide. This point of view would also explain the complete inactivity of nitrogen-free disulfides, which are naturally incapable of forming complex zinc derivatives.

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Studies on the Artificial Aging of Vulcanized Rubber

I. Depolymerization during the Heat-Aging

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Introduction

The deterioration of vulcanized rubber in contact with air is considered to be due to (1) after-vulcanization; (2) depolymerization and disaggregation, and (3) oxidation by atmospheric oxygen. Oxidation is the chief factor, and heat and sunlight (especially ultra-violet light) are considered to accelerate the process, though the mechanism is not entirely clear.

It is well known that the higher the free sulfur in vulcanized rubber the faster is the deterioration; this fact indicates that sulfur plays an important role in the deterioration process aside from its influence on aftervulcanization.

The actual extent to which depolymerization and disaggregation occur in natural aging is not clear.

Though the increase in the rate of oxidation with increase in temperature has been investigated for long time, there are good reasons for believing that physical processes as well as chemical reactions occur. Attempts have been made by the author to investigate these factors by artificial aging tests, and at the same time the rate of change of vulcanized rubber at high temperature has been studied.

The present report deals with the disaggregation phenomenon which occurs during the heat aging.

It was found that vulcanized rubber, aged in air around 70° C. for several days, gradually recovers the tensile strength lost during aging by treatment in a thermostat at −50° C. for a long time. This was found to be true of samples containing different proportions of sulfur.

Experiment 1

Ring test-pieces from vulcanized sheets were aged in an oven at 70° C. for the required time, were let stand for 24 hours after removal from the oven, and were placed in a thermostat at −50° C.; 3 test-pieces for each sample were removed after every 24 hours at −50° C. and their percentage elongations and tensile strengths determined.

Six smoked sheet-sulfur mixtures were prepared, as follows:

Sample	Sulfur	Raw Rubber	Sample	Sulfur	Raw Rubber
A	1.0	99.0	D	6.0	94.0
B	2.0	98.0	E	7.5	92.5
C	5.0	95.0	F	10.0	90.0

The results on samples containing 1 and 2 per cent sulfur were as follows:

TABLE I

Sample	Sulfur	Raw Rubber	Vulcanization Pressure (Lbs. Per. Sq. In.)	Time (Min.)	Aging (Days)	Remarks
A 1	1	99	50	120	12	Optimum cure
A 2	1	99	50	90	12	Under cure
B 1	2	98	50	120	12	Optimum cure
B 2	2	98	50	90	12	Under cure

TABLE II

Days of Aging	Cooling	Sample A 1 E.	T.S.	Sample A 2 E.	T.S.	Sample B 1 E.	T.S.	Sample B 2 E.	T.S.
0		1146*	0.419	770	0.082	1035	0.085	1127	0.727
1		1155*	0.576					1077	0.842
2		1150*	0.679					1107	1.072
3		1150*	0.725					1103	1.150
4		1143	0.736	1106	0.462			1076	1.126
5		1150	0.082					1041	0.867
7		1055	0.675					988	0.702
10		631	0.072					764	0.205
12		500	0.043	450	0.035	546	0.096	543	0.070
12	1	595	0.065	535	0.047	478	0.082	632	0.119
12	2	778	0.157	411	0.032	439	0.065	603	0.110
12	3	814	0.155	509	0.042	485	0.087	750	0.022
12	4	969	0.379	500	0.049	621	0.162	891	0.453
12	5	994	0.447	603	0.048	723	0.279	921	0.529
12	6			648	0.062	632	0.138		
12	7			986	0.366	856	0.567		
12	8			984	0.365	881	0.599		
12	9			963	0.306	888	0.603		

Remarks: E. is percentage elongation (* marks are samples which were not broken by this apparatus), T. S. is tensile strength in kg. per sq. mm.

All samples were aged at 70° C. for 12 days and then cooled. A 1 and B 2 are compared by aging and cooling curves; those of A 2 and B 1 only by cooling curves for over a prolonged period. Figure 1 shows the results with A 1 and B 2. Gradual recovery of the ultimate elongation and the tensile strength lost by 12 days of aging occurred, but the state of recovery was irregular. The recovery of A 2 by cooling reached a maximum in 7 days; further cooling showed a deterioration. The maximum recovery of the sample containing 2 per cent sulfur by cooling was smaller than the value obtained without aging. In the case of the sample containing 1 per cent sulfur, the recovered strength was far greater than that of the unaged sample, but it was less than the maximum value obtained during aging.

The results on samples containing 5, 6, and 7.5 per cent sulfur were as follows:

TABLE III

Sample	Sulfur	Raw Rubber	Vulcanization Pressure (Lbs. Per Sq. In.)	Time (Min.)	Aging (Days)	Remarks
C 1	5.0	95.0	50	90	5	Optimum cure
C 2	5.0	95.0	50	90	5	Optimum cure
D 1	6.0	94.0	50	90	8	Optimum cure
E 1	7.5	92.5	50	80	8	Optimum cure
E 2	7.5	92.5	50	80	5	Optimum cure

Figure 2 indicates the results with C 1 and E 2. Samples containing medium proportions of sulfur showed, as with those containing large proportions, irregular recovery of tensile strength by cooling, but the state of recovery was more sharply defined, and it showed a maximum point, though this maximum strength was always smaller than the control.

TABLE IV
EXPERIMENTAL RESULT

Days of Aging	Cooling	C 1 E.	T.S.	C 2 E.	T.S.	D 1 E.	T.S.	E 1 E.	T.S.	E 2 E.	T.S.
0	0	915	1.513	933	1.362	934	1.239	900	1.249	893	1.212
5	0	435	0.237	457	0.239					634	0.625
8	0					444	0.213	331	0.159		
	1	644	0.712	625	0.562	353	0.154	313	0.156	671	0.766
	2	671	0.847	686	0.731	373	0.154	347	0.178	678	0.783
	3	702	1.012	744	0.962	451	0.225	355	0.184	685	0.809
	4	677	0.877	668	0.714	526	0.352	417	0.240	703	0.942
	5			670	0.717	582	0.502	418	0.250	716	0.954
	6			605	0.528	607	0.603	622	0.717	723	1.016
	7					694	0.744	496	0.436	735	1.139
	8					516	0.286	582	0.565	735	1.111
	9					471	9.225	629	0.739	715	1.065
	10					620	0.511	615	0.730	719	0.998

The results on samples containing 10 per cent sulfur were as follows:

TABLE V

Sample	Sulfur	Raw Rubber	Vulcanization Pressure (Lbs. Per Sq. In.)	Time (Min.)	Aging (Days)	Remarks
F 1	10.0	90.0	50	30	10	Under cure
F 2	10.0	90.0	50	60	3	Optimum cure
F 3	10.0	90.0	50	60	5	Optimum cure
F 4	10.0	90.0	50	60	7	Optimum cure

TABLE VI

Days of Aging	Cooling	F 1 E.	T. S.	F 2 E.	T. S.	F 3 E.	T. S.	F 4 E.	T. S.
0	0	926	1.161	833	1.411	853	1.495	818	1.761
3	0			692	1.153				
5	0					353	2.243		
7	0							228	0.175
10	0	525	0.254						
	1/4	657	0.525						
	1	679	0.587	696	1.117	322	0.203	205	0.149
	2	596	0.372	703	1.046	326	0.205	200	0.150
	3	508	0.235	709	1.152	344	0.234	187	0.145
	4	478	0.199	671	0.957	298	0.187	178	0.133
	5	433	0.167	708	1.220	289	0.181	199	0.152
	6	436	0.155	680	0.999			188	0.143
	7	413	0.138	690	1.079			209	0.155
	8			728	1.291				

Experiments were made on both under- and optimum-vulcanized samples; those at the optimum states of vulcanization were aged to different degrees. Samples F 2, F 3, and F 4 at the optimum vulcanization showed no recovery in tensile strength by cooling, and there were indications of deterioration. On the other hand, undervulcanized sample F 1 showed a very small recovery and also a maximum point. Figure 3 indicates this relation.

Experiment 2

In Experiment 1, the aging temperature was 70° C., while in Experiment 2 the samples were aged at 85° C. They were cooled after aging as before.

TABLE VII
SAMPLES AND CONDITIONS OF VULCANIZATION

Sample	Sulfur	Raw Rubber	Vulcanization Pressure (Lb.Per Sq.In.)	Time (Min.)	Aging (Days)	Remarks
G	2	98	50	120	3	Optimum cure
H	5	95	50	90	2	Optimum cure
I	10	90	50	60	2	Optimum cure

TABLE VIII
EXPERIMENTAL RESULT

Days of Aging	Cooling	E.	G. T. S.	E.	H. T. S.	E.	T. S.
0	0	990	0.627	902	1.326	764	1.590
2	0			188	0.077	230	0.153
3	0	361	0.049				
	1	310	0.042	214	0.100	196	0.137
	2	305	0.040	293	0.136	160	0.119
	3	213	0.034	455	0.271	124	0.111
	4			400	0.210	109	0.107
	5			302	0.142	98	0.100

Sample H containing 5 per cent sulfur showed a slight recovery and gave a maximum point in the curve; while G and I deteriorated by the cooling.

Discussion of the Results

Vulcanized rubber aged at 70° C. recovered its tensile strength by cooling when it contained a very little percentage of sulfur and when it contained 5 to 7.5 per cent sulfur. It is necessary to determine whether the recovery is a result of a chemical or of a physical process before attempting to explain this phenomenon. Accordingly, untreated, aged, aged and cold-treated C 2 samples were analyzed chemically.

(A) Original untreated sample.
(B) A aged in air by heating at 70° C. for 5 days.
(C) B cooled at −50° C. for 3 days (this gave the maximum recovery of tensile strength).
(D) B cooled at −50° C. for 6 days.

Sample	A	B	C	D
Acetone extract	3.20	2.86	2.90	2.87
Chloroform extract	1.01	1.42	1.39	1.40
Free sulfur	1.73	1.35	1.35	1.35
Total sulfur	4.98	4.96	5.01	4.96

The values for A and B differ considerably, and it is evident that there is a chemical change during heat-aging, as has been found by many investigators. There is, however, no chemical change during cooling, as the values for C and D are practically the same as those for B. The phenomenon of recovery of tensile strength is entirely a physical one.

The changes which take place during heat-aging are aftervulcanization, oxidation, depolymerization, disaggregation, etc., but all except that of disaggregation, are chemical.

The terms "aggregation" and "disaggregation" were introduced by Harries.[2] Aggregation means the formation of a relatively large aggregated mass by the gathering together of rubber molecules. This is entirely different from polymerization, which involves the formation of a larger molecule out of individual molecules.

Polymerization is a chemical process, whereas aggregation is physical and reversible.

LeBlanc and Kröger[3] observed that the percentage elongation and the tensile strength of raw rubber from room temperature to −60° C. approached, with decrease in temperature, that of vulcanized rubber at room temperature. They believed that this was a vulcanization of raw rubber by physical means, and that
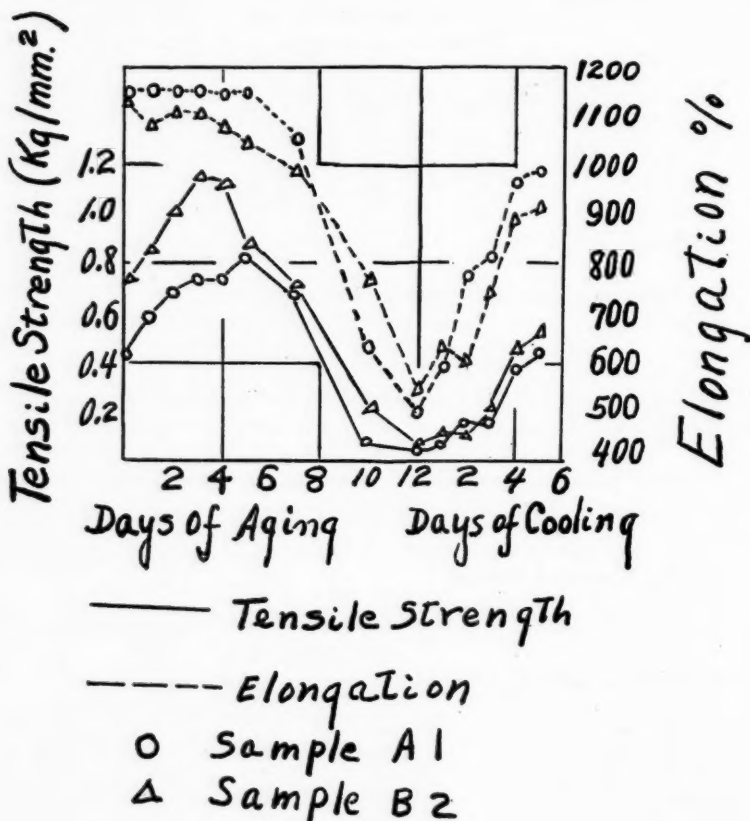

Figure 1

the principal cause of this change was aggregation. They also stated that the function of sulfur in vulcanization by heat is to bring about a physical aggregation of depolymerized rubber molecules, and in addition to this to form a chemical combination of these aggregated masses in a bridge-like structure, which prevents depolymerization by heat. Accordingly, heat-vulcanization by sulfur is irreversible, whereas physical vulcanization by cooling is reversible.

Since the recovery in tensile strength agrees well with this definition of aggregation, it seems justifiable to assume that the tensile strength lost by the heat-aging process increases by re-aggregation on cooling.

The recovery of tensile strength was greatest with rubber containing 5 to 7.5 per cent sulfur, followed by rubber containing 1 to 2 per cent sulfur. There was

practically no recovery with rubber containing 10 per cent sulfur. However, one is not justified in considering that vulcanized rubber containing higher percentages of sulfur does not depolymerize, for they may depolymerize more than those containing less sulfur, yet also oxidize and depolymerize more, and thus destroy the reversible action of disaggregation. That undervulcanized rubber showed a recovery, though only to a small extent, may be due to the fact that most of the aging effect consisted of aftervulcanization, and that reversible disaggregation was not destroyed completely. In other words, the vulcanization coefficient of insufficiently vulcanized rubber is small and is similar to that of rubber containing less sulfur, and the temperature of aftervulcanization is far lower than with a normal percentage of sulfur.

As shown by LeBlanc and Kröger, the function of sulfur during vulcanization by heat is to aggregate the disaggregated rubber molecules and further to convert them into a stable form by chemical combination. According to the theory of Axelrod[1] to explain vulcanization, rubber is first depolymerized by heat, then is polymerized by sulfur to a vulcanized state. In these two views, it is probable
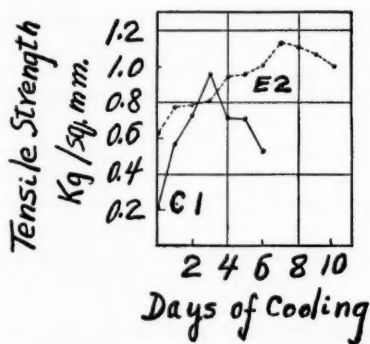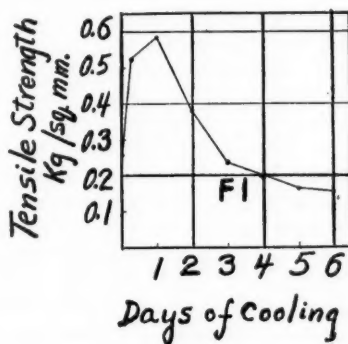

Figure 2

Figure 3

that the higher the percentage of sulfur, the greater is the stability of the product. This is at variance with the author's disaggregation theory. But, two of these views are concerned with the vulcanization process, and there is no reference to the action of heat after vulcanization or to the diminution in tensile strength by overvulcanization. The author considers that sulfur is closely related to the disaggregation process, since it is known that aging is more rapid with high sulfur contents.

The appearance of the maximum point in the tensile strength recovery curve is caused by the deterioration in the cooling process. In general, storage of vulcanized rubber at low temperatures for long periods lowers the tensile strength. This is shown by the following data.

Sample	Raw Rubber	Sulfur	Vulcanization in Steam Pressure (Lb. Per Sq. In.)	Time (Min.)
P	95	5	50	90
Q	90	10	50	60

	Sample P		Sample Q	
	Elongation (Percentage)	Tensile Strength (Kg. per Sq. In.)	Elongation (Percentage)	Tensile Strength (Kg. per Sq. Mm.)
Untreated	940	1.32	870	1.52
Cooled	888	0.93	861	1.33

The samples were kept at −50° C. for 200 hours in a "dry ice" thermostat, and the tensile strengths and the percentage elongations were determined after standing at room temperature for 24 hours.

Deterioration by storage at a low temperature for a long time may be caused by a change in the internal structure of rubber. This is, however, still uncertain. The curves of recovery of tensile strength indicate that cooling first causes aggregation, but further cooling brings about deterioration by a change of structure of the aggregated masses. Consequently rubber which showed no recovery had a tendency to deteriorate from the beginning. In general, rubber which had been aged deteriorated more than did unaged rubber.

An increase in the temperature of aging decreased considerably the recovery by cold treatment. Although there is probably more disaggregation at higher temperatures, it seems to be accompanied by more vigorous oxidation and depolymerization, and the net result is the absence of any recovery. This will be discussed elsewhere.

Summary

1. Vulcanized rubber containing 1 to 7.5 per cent sulfur recovered its tensile strength lost in heat-aging to a certain extent by chilling at a low temperature, and showed a maximum point in the curve of recovery of tensile strength.

2. Rubber containing 10 per cent sulfur showed only a slight recovery in tensile strength by cooling when undervulcanized, but under other conditions showed no recovery and deteriorated.

3. Heat-aging involves chemical reactions, whereas there is no chemical reaction during the cooling process. Therefore the recovery in tensile strength is probably a physical change caused by disaggregation, which is not only caused by heat but also through the agency of sulfur.

4. Rubber containing relatively large percentages of sulfur undergoes extensive disaggregation, but since this is accompanied by oxidation and depolymerization, there is no recovery in tensile strength.

5. The presence of a maximum point in the curve of recovery of tensile strength is attributed to a deterioration phenomenon brought about by super-cooling.

References

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II. The Relation between Aging and Temperature

It is well known that the rate of deterioration of soft vulcanized rubber in air increases with increase in the temperature of aging. In the present paper aging curves of rubber-sulfur vulcanizates at different temperatures are described, and the resulting relations between temperature and aging are discussed.

Vulcanized sheets were prepared from mixtures of 2, 5, and 10 per cent sulfur and raw rubber; each sheet was cut into rings, the latter were divided into four groups, aged in a constant temperature air bath at 55°, 70°, 85°, and 100° C. and aging curves obtained for each temperature.

Sample	Sulfur Content (Percentage)	Vulcanization Pressure (Lb. per Sq. In.)	Time (Min.)
A	2.0	50	120
B	5.0	50	90
C	10.0	50	60

The results are shown graphically in Figs. 1, 2, 3, and 4.

Each curve shows an increase in tensile strength and a maximum point, followed by a decrease, the rate of decrease becoming sudden after a certain point. The increase in tensile strength in the early stage of aging is attributable to an increase in the vulcanization coefficient by aftervulcanization. The subsequent loss is a result of oxidation, disaggregation, and depolymerization. The rapid loss of tensile strength indicates the presence of a "metamorphic point" which is a peculiar state caused by the interaction of sulfur and oxygen. Since there is no such metamorphic point in the aging curve when the aging is carried out in nitrogen gas, oxygen plays an essential part in this phenomenon.

Oxidation by atmospheric oxygen increases, of course, with increase in temperature. The sample aged at 100° C. for 24 hours showed, when stretched, the cracks indicated in Fig. 5 (No. 1 is Sample C, No. 2 is Sample B); this is due to a vigorous oxidation at the surface, which became brittle. This phenomenon was noticeable on aging above 100° C., but did not occur below 100° except after aging for a long
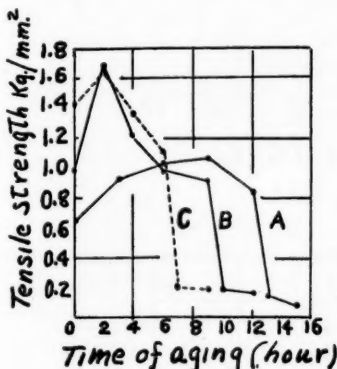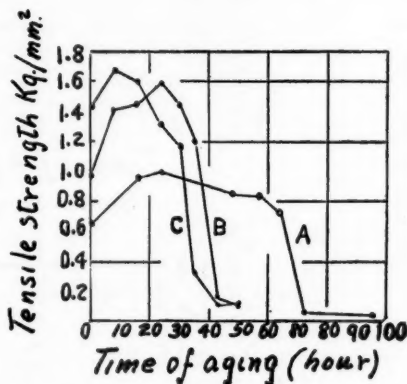

Figure 1—Aging Curves at 100° C.

Figure 2—Aging Curves at 85° C.

time. Figure 5, No. 3, is a sample aged in nitrogen gas at 100° C. No cracking was evident on the surface.

The time required to crack the surface at 100° C. was about 24 hours, but the metamorphic point appeared before this time; therefore, the oxygen necessary for this metamorphic point is probably very small. The amount of oxygen absorbed during aging cannot be estimated by ordinary analytical methods, and aging in air is attributable to the formation of a peculiar state of the rubber at the metamorphic point. The amount of direct oxidation of rubber seems to be relatively slight, and therefore this metamorphic point may be considered as an aging point. It is generally considered that aftervulcanization is a factor in aging, but is it difficult to explain why an increase in the vulcanization coefficient increases the rate of deterioration. In fact, heating in nitrogen gas at 70° C. increases the vulcanization coefficient, but does not increase the tendency to deteriorate.

The terms, *undervulcanization*, *optimum vulcanization*, and *overvulcanization*, are in common usage. By optimum vulcanization is meant not a complete combination of sulfur, but the point of maximum tensile strength, where there is still some uncombined sulfur. A further increase in the time of vulcanization decreases the tensile strength but increases the vulcanization coefficient; this is called "over-

cure" and corresponds to aftervulcanization. Raw rubber containing 10 per cent sulfur was vulcanized and the relation between the time of vulcanization and the tensile strength (vulcanization curve) was studied. The results of vulcanization with a steam pressure of 50 lbs. per sq. in. are shown in Fig. 6.
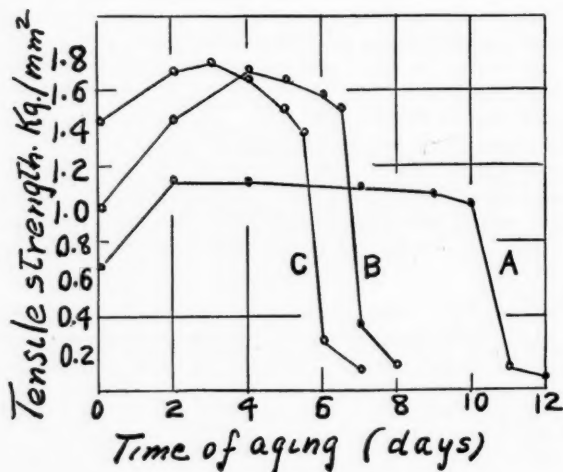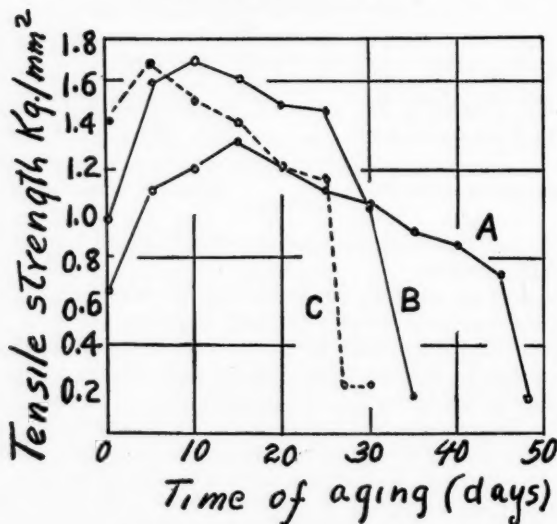

Figure 3—Aging Curves at 70° C.

Figure 4—Aging Curves at 55° C.

A vulcanization curve obtained by Numaziri[1] from a mixture of rubber, sulfur, zinc oxide, stearic acid, and diphenylguanidine gave a curve similar to that in Fig. 6.

A comparison of this curve with the aging curves in Figs. 1 to 4 shows them to be nearly alike, and the metamorphic point is evident. This means that over-

vulcanization is a part of the aging process and an increase in vulcanization coefficient is not in itself aging, but merely indicates an approach to the aging point (metamorphic point).

An increase in the temperature of aging shortens the time required to reach the aging point. The time required for deterioration of the tensile strength to 0.3 kg. per sq. mm. (this value is the time required to reach the aging point) is obtained from the curves in Figs. 1 to 4, and is shown in Fig. 7.

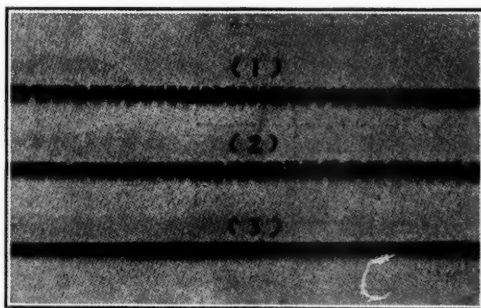The temperature t is a curvilinear function of time Z but a linear function of

Figure 5—Photographs of Samples in Elongated State

log Z. Therefore, this curve can be expressed by the general equation: $Z = ae^{bt}$, where a and b are constants. Removing log in the above equation gives log $Z = \log a + (b \log e)t$, and a and b are obtained from the mean value thus:

Constant	Sample A	Sample B	Sample C
a	225000	166000	150800
b	−0.0964	−0.0974	−0.0992

Therefore, sample A is expressible by an equation,

$$Z = 225000. \, e^{-0.0964t}$$

In a similar manner, the values of the other two samples can be obtained. Constant a depends on the kind of sample and, in this experiment, it depends on the proportion of sulfur. Since the value of a decreases with increase in sulfur, the aging time will be shortened by increase in sulfur. Constant b is a constant for temperature and is independent of the rubber or sulfur content.

In all cases the elongations at break diminished progressively with increase in the time of aging at the various temperatures.

Summary

Vulcanized samples containing 2, 5, and 10 per cent sulfur were divided into 4 groups, were aged at 55°, 70°, 85°, and 100° C. artificially in air, and aging curves obtained.

1. The deterioration of vulcanized rubber in air is attributable to the formation of a peculiar state, which is represented by a metamorphic point (aging point) in the aging curve.

2. The amount of oxygen required for the formation of this peculiar state at the

metamorphic point is very small, and direct oxidation seems to play a very small part.

3. Aftervulcanization and overvulcanization are synonymous, and an increase in vulcanization coefficient is indicative of an approach to the aging point but is not a direct cause of deterioration.

4. The time required to reach the deterioration point at a given temperature
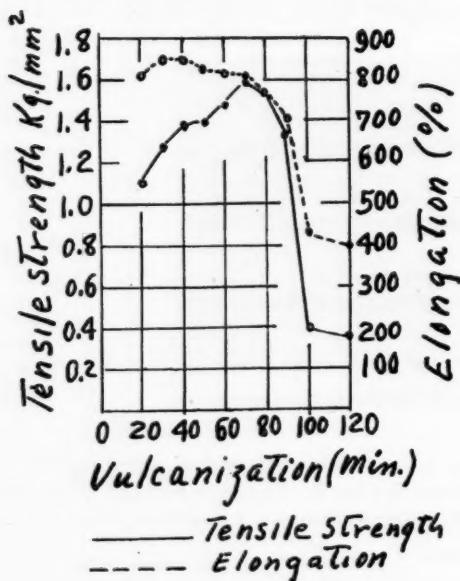
Figure 6
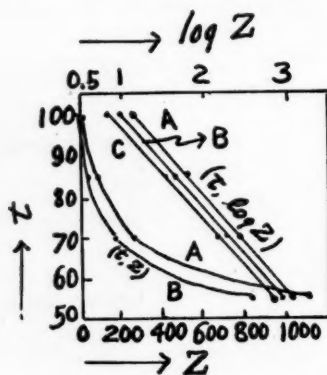
Figure 7

can be represented by the equation, $Z = ae^{bt}$, where Z is the time to reach the deterioration point, t is the temperature of aging, a is a constant depending on the type of sample, and b is a constant depending on the temperature of aging and independent of the type of sample.

III. Aging in Nitrogen Gas

It is generally recognized that oxygen has a predominant influence in the aging of vulcanized rubber in air. This influence can be realized more clearly by following aging in nitrogen gas.

Though aging in nitrogen has been investigated by Tener, Smith, and Holt[2] in 1927, the present author repeated this experiment in order to confirm whether there is a metamorphic point in the aging curve obtained with nitrogen gas. Changes in the tensile strength of samples aged in nitrogen gas by cooling to −50° C. were also determined in order to ascertain the disaggregating effect of oxygen.

Vulcanized sheets containing different percentages of sulfur as indicated in Table I were prepared, were cut into rings, and aged in nitrogen gas at 70°, 85°, and 100° C., as shown in Fig. 1.

TABLE I

Sample	Aging (Temperature C.)	Sulfur (Percentage)	Vulcanisation Pressure (Lb. per Sq. In.)	Time (Min.)
A_1	70	2	50	120
A_2	85	2	50	120
A_3	100	2	50	120
B_1	70	5	50	90
B_2	85	5	50	90
B_3	100	5	50	90
C_1	70	10	50	60
C_2	85	10	50	60
C_3	100	10	50	60

The brass aging box was coated inside with aluminum paint. The samples were hung on a glass rod.

The nitrogen was freed of oxygen by passing through hot reducing copper, and was then dehydrated by passing through phosphorus pentoxide. The air in the
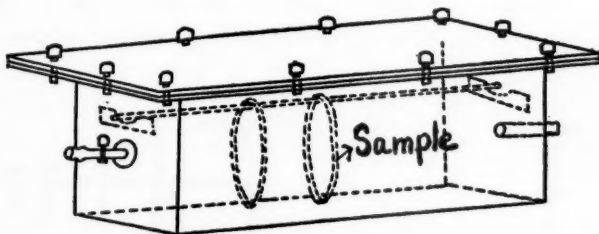
Figure 1—Aging Box

aging box was replaced by nitrogen as indicated in Fig. 2. Reservoir T for nitrogen was evacuated and the nitrogen in the bomb passed through the hot copper and into reservoir T through cooler C. The valve on the bomb was closed when reservoir T showed 1 atmospheric pressure; then the valve on T was closed. The air in aging box A was evacuated, valve V_1 was closed and nitrogen from reservoir T passed in by opening the valve attached to T. When the pressure was lowered the valve on the bomb was opened and the pressure was regulated to be always 1 atmosphere by the gage M_2. When A is filled with nitrogen gas at 1 atmosphere pressure, valve V_2 is closed. The results are shown in Tables II, III, and IV (E. is elongation; T. S. is tensile strength).

TABLE II
AGING IN NITROGEN GAS AT 70° C.

Days of Aging	Sample A_1 E.	T. S.	Sample B_1 E.	T. S.	Sample C_1 E.	T. S.
0	1065	0.619	968	1.167	833	1.198
1	1097	0.918	967	1.422	839	1.497
2	1099	0.928	967	1.441	948	1.521
4	1062	1.004	926	1.504	807	1.432
6	1025	0.981	908	1.553	782	1.425
8	1041	1.165	905	1.605	786	1.447
10	1018	1.195	887	1.611	739	1.196

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TABLE III

AGING IN NITROGEN GAS AT 85° C.

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Days of Aging	Sample A₂		Sample B₂		Sample C₂	
	E.	T. S.	E.	T. S.	E.	T. S.
0	987	0.919	877	1.233	807	1.446
2	944	1.123	758	0.932	700	1.048
4	915	0.986	716	0.827	661	0.879
6	894	0.630	686	0.614	402	0.531
8	786	0.558	500	0.450	317	0.201

<div align="center">

TABLE IV

AGING IN NITROGEN GAS AT 100° C.

</div>

Days of Aging	Sample A₃		Sample B₃		Sample C₃	
	E.	T. S.	E.	T. S	E.	T. S.
0	1065	0.619	968	1.167	833	1.198
1	1042	0.569	841	0.831	337	0.204
2	927	0.528	558	0.437	184	0.197
4	878	0.729	394	0.242	153	0.182
6	874	0.597	304	0.189	136	0.179
8	621	0.217	258	0.153	104	0.156
10	613	0.200	253	0.143	96	0.140

The values of 10 hours' aging of sample C₃ were: elongation 558, tensile strength 0.437.
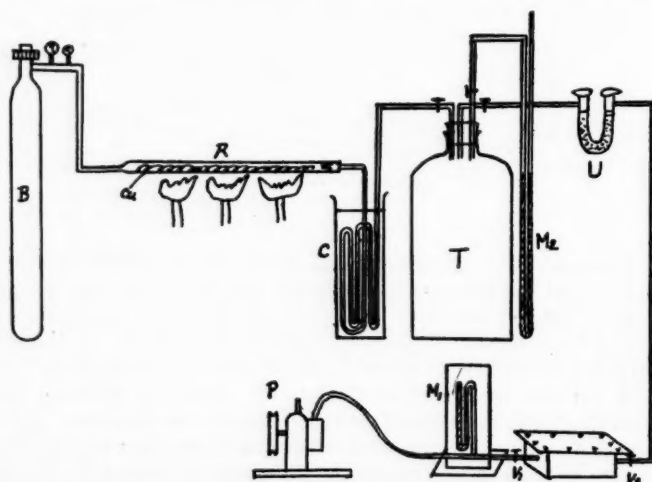
Figure 2—Apparatus for Filling an Aging Box with Nitrogen

B.	Nitrogen Bomb	A.	Aging Box
R.	Reducing Copper	P.	Vacuum Pump
C.	Cooler	M₁ and M₂.	Pressure Gauge
T.	Reservoir for Nitrogen	V₁ and V₂.	Stop-cocks
U.	U-Tube Containing Phosphorous Pentoxide		

Figure 3 indicates the results of aging at each temperature with sample B. The same result was obtained with samples A and C. Treatment in nitrogen at 70° increases the tensile strength as a result of aftervulcanization; at 85° and at 100° there was considerable deterioration, though the rates of deterioration at these temperatures were far less than by aging in air. In the experiments of Tener and his co-workers on aging in commercial nitrogen at 70°, 80°, and 90° C., there was practically no deterioration at 70° and 80°, but considerable at 90°.

Consequently aging below 80° is caused principally by oxygen, and though the elevated temperature accelerates the reaction with oxygen, this is not a direct course of deterioration. Above 80°, the rate of reaction with oxygen is not only increased, but thermal decomposition or a change in structure of the rubber also takes place.

There is no metamorphic point in the aging curve (tensile strength vs. time of aging) with nitrogen gas; therefore, the presence of oxygen is necessary for the formation of a metamorphic point (aging point).

Changes in tensile strength after cooling of rubber aged in nitrogen may throw light on the mechanism of deterioration in nitrogen at elevated temperatures.
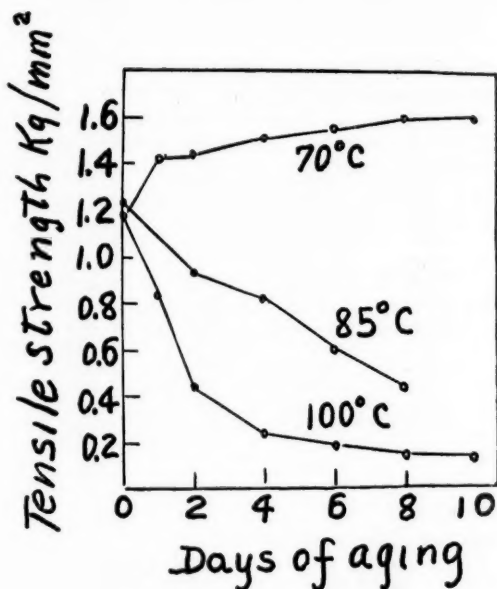
Figure 3
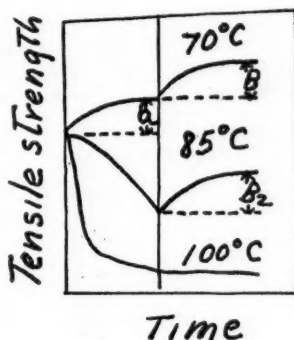
Figure 4

The testing methods in the cooling experiments were the same as in the earlier work, the temperature being −50° C.

It has already been mentioned that rubber aged in nitrogen at 70° C. increases in tensile strength as a result of aftervulcanization but its tensile strength increases further by cooling. Samples containing 2 and 5 per cent sulfur increased in tensile strength by cooling but that containing 10 per cent sulfur did not. Samples aged at 100° C. showed no recovery in tensile strength by cooling, regardless of their sulfur content. The changes in sample B by aging at various temperatures of aging and cooling is shown in Fig. 4, in which a is the increase in tensile strength by vulcanization, and b_1 and b_2 are increases in tensile strength by aggregation during cooling of samples depolymerized by heating.

The absence of recovery in tensile strength of samples aged in nitrogen at 100° C. is attributable to irreversible depolymerization. The fact that the maximum tensile strength recovered after aging at 85° C. is lower than that of the original sample suggests depolymerization as well as disaggregation. This depolymerization occurs only above 80° C.

TABLE V

Sample	Temperature of Aging C.	Days of Aging	Sulfur (Percentage)	Vulcanization Pressure (Lb. per Sq. In.)	Time (Min.)
A$_4$	70	31	2	50	120
A$_5$	85	14	2	50	120
A$_6$	100	8	2	50	120
B$_4$	70	16	5	50	90
B$_5$	85	6	5	50	90
B$_6$	100	4	5	50	90
C$_4$	70	12	10	50	60
C$_5$	85	7	10	50	60
C$_6$	100	1	10	50	60

TABLE VI

AGING-COOLING (NITROGEN AT 70° C.)

Days of Cooling		Sample A$_4$ Aged 31 Days		Sample B$_4$ Aged 16 Days		Sample C$_4$ Aged 12 Days	
		E.	T. S.	E.	T. S.	E.	T. S.
Original	0	1003	0.611	952	0.951	833	1.113
Aged	0	923	0.724	871	1.227	771	1.349
	1	896	0.770	891	1.373	768	1.369
	2	921	0.929	897	1.406	770	1.399
	3	915	0.880	881	1.306	767	1.330
	4	908	0.889	901	1.398	768	1.389
	5	933	0.987	904	1.414	768	1.422
	6	936	0.908	890	1.391	759	1.343
	7	925	0.919	902	1.518	762	1.374
	8	940	0.923	883	1.381	762	1.393
	9	938	0.972	878	1.351	777	1.399
	10	950	1.039	889	1.449	766	1.434
	11	...	...	886	1.334	797	1.513

TABLE VII

AGING-COOLING EXPERIMENT (NITROGEN AT 85° C.)

Days of Cooling		Sample A$_5$ Aged 14 Days		Sample B$_5$ Aged 6 Days		Sample C$_5$ Aged 7 Days	
		E.	T. S.	E.	T. S.	E.	T. S.
Original	0	990	0.627	902	1.326	764	1.590
Aged	0	880	0.764	710	0.862	235	0.204
	1	876	0.652	718	0.895	230	0.197
	2	890	0.780	720	0.923	255	0.221
	3	889	0.740	725	0.926	249	0.216
	4	896	0.785	723	0.945	245	0.214
	5	896	0.802	719	0.989	254	0.218

TABLE VIII

AGING-COOLING (NITROGEN AT 100° C.)

Days of Cooling		Sample A$_6$ Aged 8 Days		Sample B$_6$ Aged 4 Days		Sample C$_6$ Aged 1 Day	
		E.	T. S.	E.	T. S.	E.	T. S.
Original	0	1069	0.727	940	1.237	838	1.383
Aged	0	875	0.445	427	0.197	420	0.279
	1	897	0.468	444	0.211	410	0.271
	2	894	0.483	431	0.234	395	0.251
	3	840	0.395	443	0.217	387	0.257
	4	835	0.387	451	0.221	397	0.264
	5	846	0.399	456	0.218	425	0.295

The considerable tendency of rubber to disaggregate by aging in air at 70° C. in comparison with the disaggregation of rubber aged in nitrogen shows that oxygen plays an important role in the disaggregation process, wholly aside from the action of sulfur. Therefore, deterioration around room temperature is due principally to disaggregation caused by oxygen and direct oxidation plays a minor role. Deterioration at elevated temperatures is caused by oxygen and depolymerization by heat. Depolymerization and disaggregation take place to the greatest extent at the aging point (metamorphic point).

Summary

1. Aging in nitrogen results in very little deterioration below about 80° C., whereas deterioration is rapid above this temperature.

2. There is no metamorphic point in the curve representing aging in nitrogen.

3. During aging in air below 80° C., disaggregation is brought about by oxygen, aside from an independent effect of sulfur; above this temperature depolymerization takes place through the agency of heat. Depolymerization and disaggregation are most rapid at the metamorphic point.

References

[1] Numasiri, *J. Soc. Chem. Ind. Japan*, **39**, 136 (1936).
[2] Tener, Smith, and Holt, *Bureau of Standards, Tech. Paper* No. **342**.

The Errors in Tensile Strength Testing

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RUBBER SERVICE LABORATORIES, IMPERIAL CHEMICAL INDUSTRIES, LTD.

It is recognized that the determination of the breaking stress of vulcanized rubber can be subject to appreciable error. For this reason it is not generally considered sufficient to break one specimen only from each piece of rubber to be tested. Several specimens cut from the same piece are usually broken. From these several results an estimate of the "correct" result is made. The methods of making this estimate vary from laboratory to laboratory.

Some laboratories (Cotton and Barton, *Trans. Inst. Rubber Ind.*, **7**, 67 (1931)) prefer to regard the maximum value obtained as the most reliable, rejecting all the lower values. This attitude is based on the view that all possible errors in the determination are such as to give low values. If this assumption could be shown to be justified, the practice would have much to commend it, although, unless it could also be shown that appreciable errors were infrequent, it would still have the serious practical disadvantage that the extent of the error of the highest of a comparatively small number of results would remain completely unknown, and would vary considerably.

The diametrically opposite viewpoint that the observed variations should be regarded from the point of view of the usual theory of errors has recently been re-advocated by Reece (*Trans. Inst. Rubber Ind.*, **11**, 312 (1935)).

Various methods commonly adopted represent a compromise between these two viewpoints. In some laboratories any "obviously" low results are rejected and the mean of the rest taken. In others all results within 10 per cent of the highest are averaged.

The latter method could be justified on the assumption that the majority of the results obtained were randomly distributed about a mean in accordance with the laws of chance, while a minority of the results were affected by exceptional errors resulting in low breaking stress. If this is a true picture of the position in tensile strength testing, then it will be possible, by methods to be discussed later, to distinguish these exceptional results, and to obtain the best estimate of the breaking stress of the material which the data are capable of furnishing by averaging the remaining values.

Reece (*loc. cit.*) discusses the data obtained by Wiegand and Braendle (*Ind. Eng. Chem., Anal. Ed.*, **1**, 113 (1929)) on 95 dumb-bell shaped test-pieces on a standard Scott machine, and by Fric (*Chemie et Industrie*, Special No., April, **1928**, 541) on 730 ring test-pieces on a Schopper machine.

From a comparison of the distributions of these two sets of data with the normal probability curve he concludes, as did the authors of the data, that the breaking of a test-piece is essentially an event governed by the laws of chance, and that therefore some form of average value and not the maximum value of a set of data should be selected.

The fact that the distributions of the results in neither case exactly fit the normal probability curve, but exhibit a skew form due to an excess of low values, in no way invalidates this conclusion.

The present authors have carried out an analysis of the records of tests of ring specimens made on a Schopper machine in the Rubber Service Laboratory of Imperial Chemical Industries, Ltd. The results entirely confirm the conclusions drawn from the data of Wiegand and Braendle (*loc. cit.*) and Fric (*loc. cit.*).

The results which we have examined were obtained in the course of the routine testing work of the laboratory on over 200 different experimental rubber mixes. Six test rings were cut and broken from each rubber piece. For each of these sets of six tests the mean and the range were calculated. The range is obtained by subtracting the lowest result from the highest.

Owing to the considerable variations in the compositions of the different experimental mixes, the means of the different sets of results naturally varied considerably. The sets were therefore divided into the following groups:

Group 1. Sets with means greater than 200 kg. per sq. cm.
Group 2. Sets with means between 150 and 200 kg. per sq. cm.
Group 3. Sets with means between 100 and 150 kg. per sq. cm.
Group 4. Sets with means less than 100 kg. per sq. cm.

An approximate estimate of the standard deviation of a single test result for sets within each of these groups was calculated by the mean range method (Pearson and Davies, *J. Roy. Statis. Soc. Ind. & Agric. Supplt.*, 1, 76 (1934)). These estimates did not differ significantly. It was therefore considered justifiable to treat all the sets of observations together. The whole of the data were combined by superimposing the means of each set to form the histogram shown in Fig. 1, in which each single test result appears as a positive or negative deviation from the mean of the set of six results of which it forms a part. This histogram is closely similar to those representing the results of Wiegand and Braendle and of Fric, and is sufficient to justify the use of some form of average value. It exhibits a large tail on the negative side, showing the presence of a number of exceptionally low results.

A simple average will therefore generally be biased and the bias will most frequently be such as to lead to too low an estimate of the breaking stress. The same conclusion was drawn by Wiegand and Braendle from their results. Fric considered his results to be distributed sufficiently closely to a normal probability curve to justify the use of an uncorrected mean. Fric's results do, however, show a slight negative tail. When replotted by Reece, this negative tail is almost as great as that of Wiegand and Braendle's results, so that it may be concluded that these data also show that a simple average is not satisfactory. The extent of the error caused by the use of a simple average may well vary from laboratory to laboratory.

All the above authors appear to account for the excess of low results by assuming that some faults (by implication some exceptional faults) are present in some of the test-pieces. They do not, however, follow this very reasonable assumption to its proper conclusion when seeking methods to correct the simple average. A method is required which will pick out the exceptional results, leaving the remainder to be averaged. The number of such exceptional results in a set of five or six tests on specimens from one piece of rubber will vary. The procedure recommended by Wiegand and Braendle of averaging the three highest of five results always rejects two of the five, though often only one, or none at all, should be rejected, and it will occasionally cause a figure to be recorded with confidence when the five results are such that a repeat test is necessary.

The arbitrary rule involving rejection of all results more than 10 per cent below the highest is better, as it takes account of the spread of the results and will obviously cause a set of five or six results to be suspect when its application leads to rejection of all but one or two.

An exact procedure can be reached if the standard error of a single normal test is known. By a normal test is meant any test other than the exceptional few which are to be rejected.

The authors have calculated the standard error of normal tests for the data from which the histogram of Fig. 1 was prepared, in the following manner.

In most of the 205 sets of tests analyzed, the number of tests was six, but in a few the number of tests was less than six owing to accidental causes. The ranges of all sets of six tests were added. Let the sum be Sw_6. Similarly the ranges of all sets of five tests were added. Let the sum be Sw_5. In the same way Sw_4 and Sw_3 were calculated. Then an estimate of the standard error of individual tests is given by the formula

$$s_1 = (0.3946\ Sw_6 + 0.4299\ Sw_5 + 0.4857\ Sw_4 + 0.5908\ Sw_3)/N \qquad \text{(I)}$$
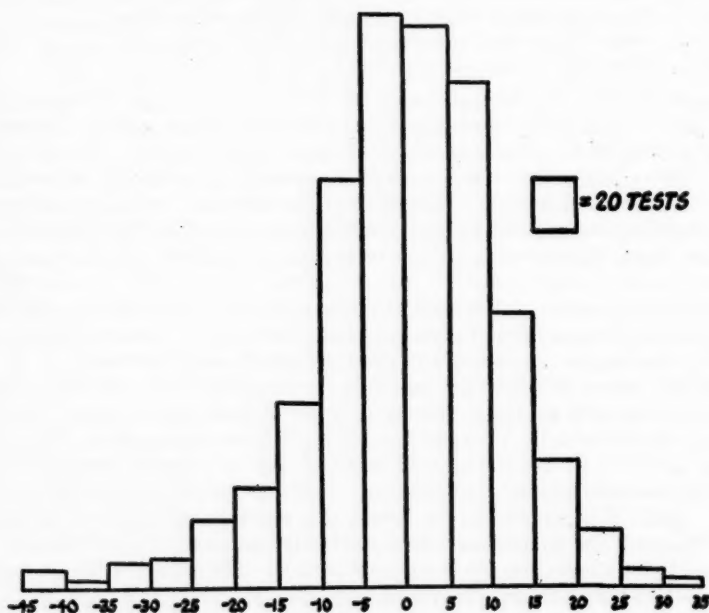
Figure 1—Deviation from Mean (Kg. Per Sq. Cm.)

where N is the total number of sets (in this case 205). The coefficients of Sw_6, Sw_5, etc., are given by Pearson and Davies (*loc. cit.*). Expression (1) reduces to

$$s_1 = \frac{2295.95}{205} = 11.20$$

The estimate of the standard error s_1 is high owing to the inclusion of the exceptional results, but it provides a measure which can be used to eliminate the worst of these results. The calculation can then be repeated, ignoring the eliminated results, and a more correct estimate s_2 obtained. A further elimination and recalculation will give a nearly correct estimate s_3.

The method adopted to eliminate the exceptional results consisted of examining each set and striking out any points which lay outside the range (mean ± 30). 30

= 2.7 s_1 = 3.3 s_3, so that the chance of rejecting a result which ought to have been retained was less than one in one thousand. s_3 was found to be 9.0. This method of calculating the standard error from the ranges of the sets of tests was adopted owing to its simplicity, and the small amount of arithmetical work involved, particularly as the calculation had to be repeated until the exceptional results were eliminated.

The standard error was finally calculated by the most efficient method (R. A. Fisher, *Statistical Methods for Research Workers*) from the formula

$$s^2 = S \left[S_i \, (x_{ti} - x_t)^2 \right] / S_t (n_t - \mathrm{I})$$
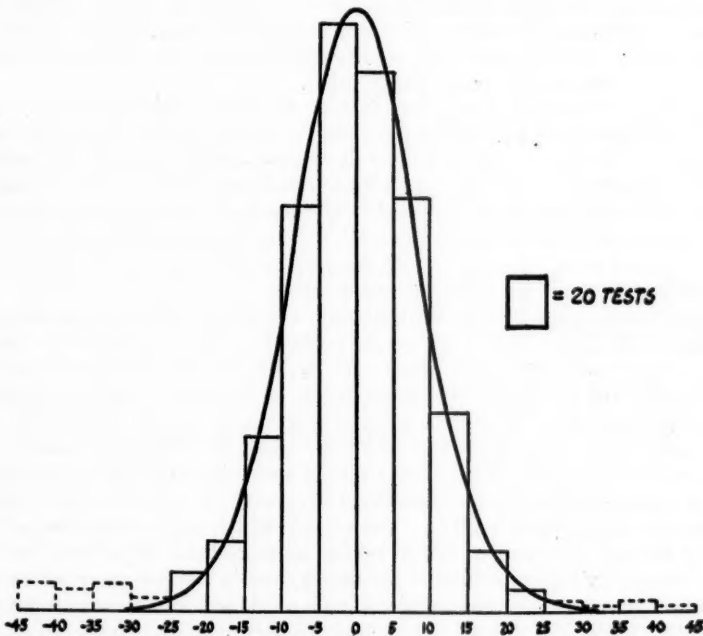
Figure 2—Deviation from Mean (Kg. Per Sq. Cm.)

after neglecting the results eliminated above. x_{ti} is the ith test in the tth set, x_t is the mean of the tth set, and n_t is the number of tests in the tth set. S denotes the summation of all quantities of the type in the brackets following the symbol.

The result of this calculation was

$$s^2 = 83.282 \text{ or } s = 9.13$$

This estimate of the standard error of a single test does not differ significantly from the estimate $s_3 = 9.0$ found above by the much more rapid and less laborious calculation from the ranges of the sets. The agreement affords further confirmation of the reliability of the range method.

A histogram was again constructed by superimposing the means of the 205 sets of results, recalculated after elimination of the exceptional points. This histogram is shown in Fig. 2, together with the normal probability curve which fits it. The total area under the curve is equal to the total area under the histogram. The ex-

ceptional results which had been eliminated are shown by the rectangles drawn in broken line. It will be seen that a few exceptionally high results were obtained, as well as a number of exceptionally low results.

It is now necessary to consider what rule to adopt for the rejection of exceptional results when dealing with small sets of five or six tests on any one specimen of rubber. Any rule which is devised may err in two ways: (*a*) it may fail to reject all the abnormal results, or (*b*) it may cause the rejection of a result which should be retained.

The more stringent the rule the less the chance of error (*a*), but the greater the chance of error (*b*). For practical purposes it will suffice if the chance of rejection of a result which should be retained is reduced to as little as 1 in 20. This will be achieved by rejecting all results which fall outside the range (mean ± twice the standard error). In the case of the results considered above this involves the rejection of results outside the range (mean ±18).

In applying this method of rejection, it must be remembered that an appreciable number of exceptionally low results have been shown to occur. One or more such results may be present in a set of five or six tests, and their presence will cause the mean first calculated to be low, and might occasionally lead to the unjustifiable rejection of the highest result of the set. If, therefore, the first application of the method to the set of five or six results rejects one or more exceptionally low results and also appears to reject a high result, the high result should not be rejected until the method is again applied using the new mean.

The rule then in practice can be formulated as follows: Calculate the mean of a set of five or six tests. Reject all results lower than mean by twice the standard error of a test. Recalculate the mean of the results not rejected above. Reject all results which now lie outside the range (mean ± twice the standard error), and average the remainder. The application of this rule to sets of five or six tests has been found often to reject none, and seldom to reject more than two results.

It is clear that any rule which always rejects a certain number of results, such as that of Wiegand and Braendle which rejects the lowest two of a set of five, will often reject results without justification. Even a rule which takes some account of the spread of the set, such as that which rejects all more than 10 per cent below the highest, frequently rejects results unjustifiably, and in the few cases where an exceptionally high result has been obtained, such a rule will lead to serious error.

The standard error of a single test is likely to vary somewhat from laboratory to laboratory, even if results obtained on a Schopper machine only be considered, as it includes variations from part to part of the piece from which the six test rings are cut, and this variation depends on the degree of uniformity of mixing and on the degree of uniformity of the conditions in the press during cure. Anyone can however readily calculate the error appropriate to their conditions from ordinary data accumulated in the course of routine work of the laboratory by the range method described above.

The calculation of the standard error of a test also enables an estimate to be obtained of the accuracy of the mean of a number of tests. The standard error of a mean of n tests is equal to the standard error of a single test divided by $\sqrt{n}$. For the data analyzed above the standard error of a mean of six tests is $9/\sqrt{6} = 3.77$. The odds are then 19 to 1 that a mean of six tests does not differ by more than twice this amount, *i. e.*, 7.5, from the mean which would have been obtained from a very large number of tests. Similarly, in comparing the mean of a set of n_1 tests with the mean of a set of n_2 tests, the standard error of the difference between the two means is given by

$$s\sqrt{\frac{1}{n_1}+\frac{1}{n_2}}$$

where s is the standard error of a single test.

When both n_1 and $n_2 = 6$ this becomes $s\sqrt{\frac{1}{3}}$

The two means can be considered to differ for reasons other than the experimental error of the test when the difference between them exceeds $2s\sqrt{\frac{1}{3}}$. For the above data $2s\sqrt{\frac{1}{3}} = 10.3$. Differences smaller than this must be attributed to experimental error.

Summary

The conclusions drawn from the data of Wiegand and Braendle and of Fric that the breaking of rubber during tensile strength testing is essentially an event governed by the laws of chance, and that therefore some form of average is the only appropriate method of estimating the "correct" result from a number of tests is supported by the nature of the data obtained in routine testing in the rubber service laboratories.

The presence of an excess of abnormally low values and of a few high values is also confirmed. After calculating the standard error of a test, a rule has been devised for eliminating abnormal results before averaging the remainder. This rule is to be preferred to any of the various arbitrary rules hitherto in use.

Nonsolvents in Rubber Cements

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ETHANOL has long been used for reducing the apparent viscosity of rubber cements. Other rubber nonsolvents, especially acetone and amyl acetate, are sometimes similarly employed. However, there are few data in the literature from which adequate comparisons among nonsolvents may be deduced, nor has any systematic study of the properties of a cement containing nonsolvents been reported.[1] Whitby (2), studying a long list of chemicals as solvents, records comparative swelling power for rubber and nitrocellulose; Whitby and Jane (3) find the viscosity of dilute rubber solutions to be reduced by a number of these materials; and Kawamura and Tanaka (1) obtain the following order of decreasing precipitant value for a 0.25 per cent solution of rubber in xylene—methanol, ethanol, n-butanol, isobutanol. With the exception of the swelling experiments, these results, as is the case with practically all published cement studies, are for dilute solutions only and therefore are of little technical value.

The present experiments were performed with a commercial cement and are the result of a wish to control particularly two properties—the thickness of rubber film deposited upon an article by dipping and the tendency of the wet film to break across small holes in perforated objects. The addition of a suitable nonsolvent to a cement improved the film-breaking property, and by changing the proportion of the nonsolvent, with proper regard for other factors, satisfactory control of both film breaking and film thickness was possible. As here reported, the results afford a basis for comparison among the more common nonsolvents in cements in which the solvents used are benzene, Varnish Makers and Painters' (V. M. & P.) naphtha, or ethylene dichloride; and for a benzene-isopropanol cement they show the nature of the effects upon the properties studied, of simultaneously varying the proportion of nonsolvent, the concentration of nonvolatile ingredients, and the degree of mastication of the rubber stock. Results on temperature and humidity control are included to illustrate the importance of these factors in dipping-room operations.

The nonvolatile ingredients of the cement used in these studies were as follows (in grams):
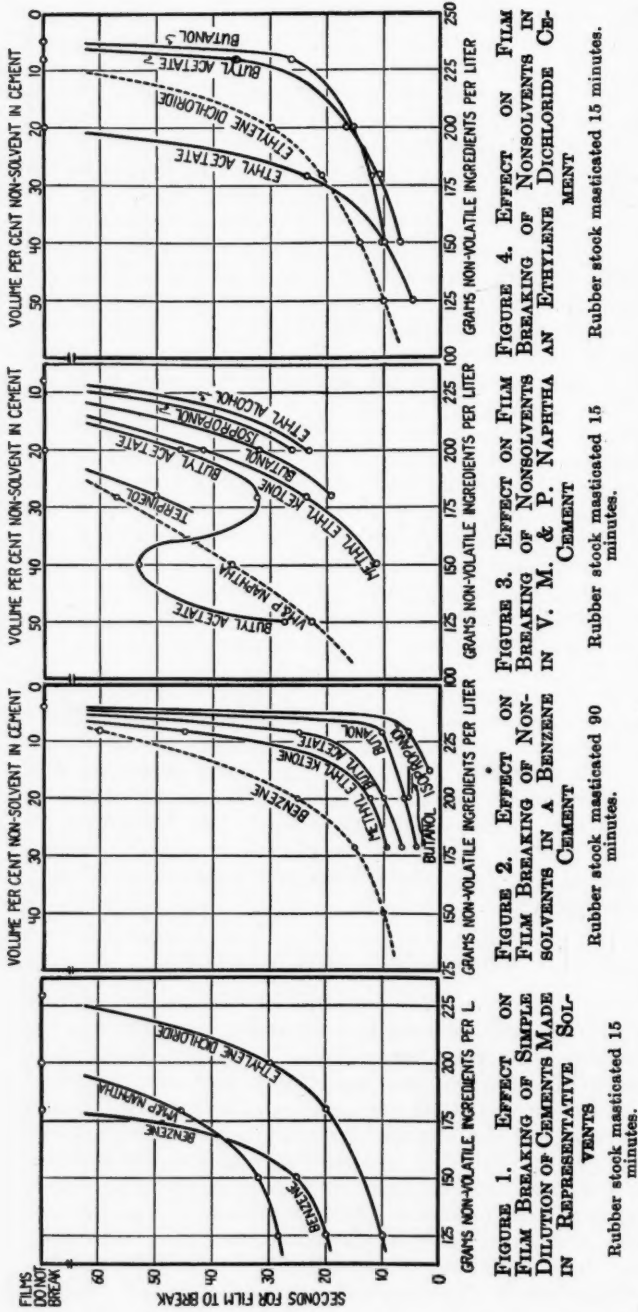
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[1] Since this paper was written, Fabritziev et al. [*Kozhevenno-Oburnaya Prom.*, **14**, 514–18 (1935)] have reported experiments on the same nonsolvents used here.

Rubber (pale crepe)	100	Carbon black	5
Sulfur	60	Mineral oil	50
Clay	52	Aldehyde-amine accelerator (liquid)	2

Despite the specific nature of this recipe the results are not limited in their significance, since the properties of a cement generally are influenced far more by the concentration and kind of rubber present than by pigment loading. For the experimental work, cements containing solvent but no nonsolvent, were prepared in laboratory churns, and the measurements were made upon aliquot parts to which varying proportions of the nonsolvents were added. All cements were prepared under comparable conditions, and each set of experiments was performed at one time, so that errors due to temperature and humidity variations are negligible. The rubber stocks for the various cements were all mixed on the same laboratory mill by the same operator, and a definite procedure was followed. All of the nonvolatile ingredients except the mineral oil were mixed on the mill, and the oil was added in the churn. The time of mastication was measured from the start of breakdown of the rubber. Film thickness was calculated from the dry weight and the area of a deposited film; and the film-breaking tendency was measured as "film-breaking time," in seconds required for a standard film to break or as "per cent break"—i. e., the number of films breaking per hundred standard films formed over small holes in a perforated panel, as explained in detail later. The experimental results are presented in the order in which they were obtained, falling into three groups: (a) the comparative effectiveness of various nonsolvents in causing film breaking; (b) the effects upon film thickness and film breaking of varying the proportion of nonsolvent, the concentration of nonvolatile ingredients, and the degree of mastication of the rubber stock for a benzene-isopropanol cement; and (c) the effects of temperature and humidity upon these properties.

Comparison of Nonsolvents

Since nonsolvents are useful in cements because of their effect upon film breaking, this property was employed as the basis for comparison among them. To cements prepared as previously described, the nonsolvents were added stepwise and film-breaking time was measured. In these experiments the standard film was that formed over a small round hole (0.63 cm. in diameter) centered 0.63 cm. from one end of a 5 × 12.5 × 0.078 cm. iron panel. Panels were dipped to a depth of 5 cm. in cements free from air bubbles or scum, and were withdrawn slowly at a standard rate. Time was measured from the instant of withdrawal of the film through the cement surface. Three solvents studied (benzene, V. M. & P. naphtha, and ethylene dichloride) were considered the most representative of the aromatic, the aliphatic, and the com-

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FIGURE 1. EFFECT ON FILM BREAKING OF SIMPLE DILUTION OF CEMENTS MADE IN REPRESENTATIVE SOLVENTS

Rubber stock masticated 15 minutes.

FIGURE 2. EFFECT ON FILM BREAKING OF NONSOLVENTS IN A BENZENE CEMENT

Rubber stock masticated 90 minutes.

FIGURE 3. EFFECT ON FILM BREAKING OF NONSOLVENTS IN V. M. & P. NAPHTHA CEMENT

Rubber stock masticated 15 minutes.

FIGURE 4. EFFECT ON FILM BREAKING OF NONSOLVENTS IN AN ETHYLENE DICHLORIDE CEMENT

Rubber stock masticated 15 minutes.

mercial chlorinated solvents, respectively. In cases where combinations of solvents within a homologous series are desirable for control of evaporation rate, it is probably safe to assume that the present results will hold for the combination about as well as for the single solvents studied here.

Effect of Simple Dilution on Film-Breaking Time

The effect of simple dilution upon film-breaking time for cements made in benzene, V. M. & P. naphtha, and ethylene dichloride is shown by Figure 1. Within the concentration range studied, ethylene dichloride is evidently a much more powerful solvent than either of the others, if by solvent power is meant ability to dissolve a large amount of rubber to form a cement of low apparent viscosity. There seems to be com-

FIGURE 5. FILM-BREAKING CHARACTERISTICS OF A BENZENE-ISOPROPANOL CEMENT AT DIFFERENT CONCENTRATIONS OF RUBBER AND ISOPROPANOL

Rubber stock masticated 90 minutes.

paratively little difference between benzene and V. M. & P. naphtha. However, different orders of solvent power may be obtained, depending upon the viscosity (film breaking) desired, because the two curves cross each other. It is not correct to assume that the properties of a cement always vary with dilution in the same way regardless of solvent. Obviously, the choice of solvent may sometimes be greatly influenced by the particular combination of concentration and flowing qualities desired in a cement.

Effectiveness of Nonsolvents in Benzene Cement

Figure 2 shows the nature of the changes in film-breaking time as a benzene cement is diluted with various nonsolvents.

These curves were obtained by successive additions of non-solvent to a benzene cement originally containing 250 grams of nonvolatile ingredients per liter of cement. For comparison, a blank curve shows the changes on simple dilution of this cement with benzene. All of the nonsolvent curves terminate at the last value obtained before coagulation of the cement occurred. These curves show, therefore, not only effects upon film breaking, but the relative tolerance of a benzene cement for the different nonsolvents as well. Upon the basis of this diagram and of supplementary data for benzene cements and concentrations of diluent between 10 and 20 volume per cent, the various liquids can be arranged in the following order of decreasing effectiveness in film breaking: isopropanol,
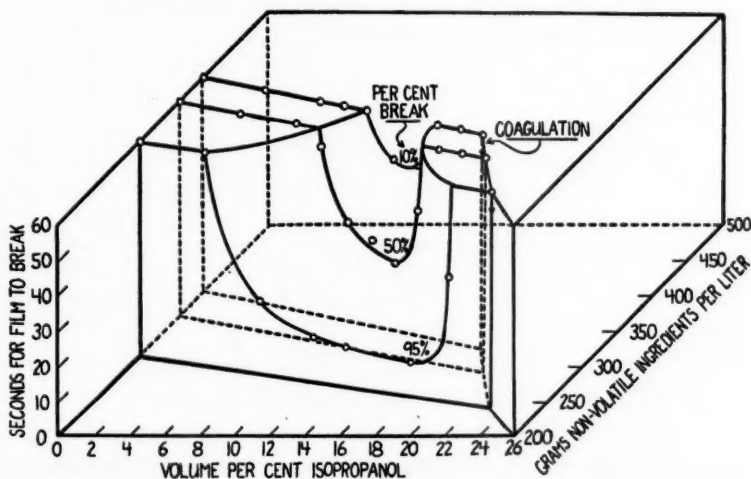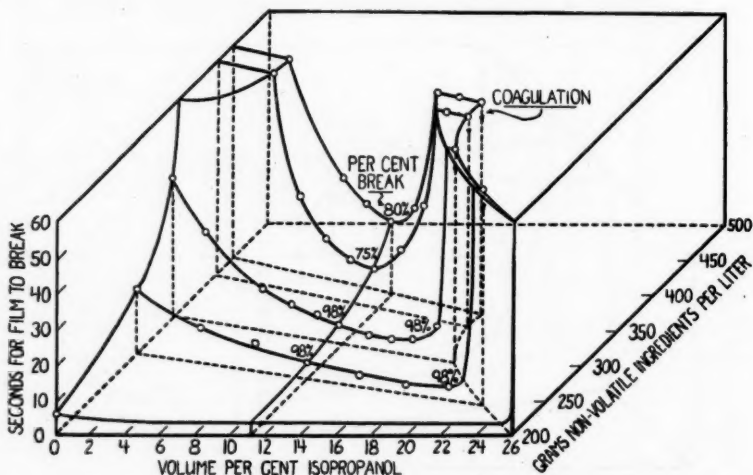

FIGURE 6. FILM-BREAKING CHARACTERISTICS OF A BENZENE-ISOPROPANOL CEMENT AT DIFFERENT CONCENTRATIONS OF RUBBER AND ISOPROPANOL

Rubber stock masticated 11.75 hours.

ethanol, Pentasol (technical grade), butanol (technical grade), amyl acetate, butyl acetate, acetone, methyl ethyl ketone, benzene.

Although there is actually almost no difference between isopropanol and ethanol in volume-for-volume effect on film breaking, the tolerance for ethanol is much less than for isopropanol. If over 10 per cent of ethanol is used, coagulation occurs, whereas more than 15 per cent of isopropanol may be present without coagulation. In deposited films, the simultaneous evaporation of benzene and ethanol apparently causes wide variations in alcohol content so that films sometimes break and sometimes do not. With isopropanol this trouble is not encountered.

Branching from the isopropanol curve in Figure 2 is a horizontal line marked "butanol." This means that, after dilution of the cement with isopropanol to this point, butanol was added. The curve shows that the further dilution with butanol gave no further change in film breaking until a total dilution was reached where a change would have occurred had the entire dilution been with butanol alone. It is also interesting that the curve for dilution with V. M. & P. naphtha falls somewhat above the curve for benzene. The practical conclusion from this latter observation is that cements which have lost solvent by evaporation should be "made up" only with the solvent originally present.

Effectiveness of Nonsolvents in V. M. & P. Naphtha Cement

Figure 3 is similar to Figure 2 and was obtained by successive additions of nonsolvent to a V. M. & P. naphtha cement originally containing 250 grams of nonvolatile ingredients per liter of cement. Upon the basis of this diagram, for V. M. & P. naphtha cements the order of decreasing effectiveness in film breaking for concentrations of nonsolvent between 10 and 20 volume per cent is: ethanol, isopropanol, butanol, methyl ethyl ketone, butyl acetate, V. M. & P. naphtha.

Approximately 20 per cent of ethanol can be added to a V. M. & P. naphtha cement, in contrast to the maximum of 10 per cent which can be added to a benzene cement. From the standpoint of tolerance, therefore, ethanol is evidently as good as isopropanol in gasoline cements.

Effectiveness of Nonsolvents in Ethylene Dichloride Cement

Figure 4 is similar to Figures 2 and 3. Upon the basis of this diagram for ethylene dichloride cements for concentrations of nonsolvent between 10 and 20 volume per cent, the order of decreasing effectiveness in film breaking is: butanol, butyl acetate, ethylene dichloride, ethyl acetate. Ethanol, acetic acid, dichlorodiethyl ether, methyl ethyl ketone, and isopropanol merely cause coagulation.

Simultaneous Control of Film Thickness and Film Breaking

The important factors in the control of the properties of a rubber cement are: the proportion of nonsolvent in the liquid system, the concentration of nonvolatile ingredients, and the degree of mastication of the rubber stock. For the study of the effects upon film thickness and film breaking of varying these three factors simultaneously, the benzene-isopropanol solvent mixture was selected. In the experimental work it was found desirable to supplement "film-breaking time" by measurement of "per cent break." For this purpose small aluminum panels, 0.157 cm. thick and

carefully drilled with one hundred holes 0.48 cm. in diameter, evenly spaced on 0.73-cm. centers, were employed. These panels were slowly withdrawn from the cements and the number of holes over which the films broke were recorded as "per cent break." For the measurement of average film thickness, $5 \times 12.5 \times 0.078$ cm. iron panels were immersed in the cements to a depth of 10 cm. and withdrawn slowly at a uniform rate, the dry weight of the deposited film being found by difference.

Optimum Per Cent Isopropanol

Figures 5 and 6 show the relations between concentration of nonvolatile ingredients, volume per cent isopropanol, and film breaking for benzene cements made from rubber stocks masticated 1.5 and 11.75 hours, respectively. Diagrams for intermediate mastication times are similar. The valleys

FIGURE 7. RELATION OF FILM THICKNESS AND PER CENT BREAK TO MASTICATION OF RUBBER STOCK AND CONCENTRATION OF CEMENT FOR A BENZENE CEMENT CONTAINING 11.2 PER CENT BY VOLUME OF ISOPROPANOL

represent the areas where maximum film breaking occurs. Evidently for this cement, regardless of concentration of nonvolatile ingredients or of time of mastication, the maximum film-breaking effect is obtained when the cement contains about 11 per cent by volume of isopropanol.

Correction of Film Thickness

Although the film-breaking properties of a cement are greatly improved by adding isopropanol, film thickness is at the same time reduced. This effect can be offset by increasing the mastication time of the ru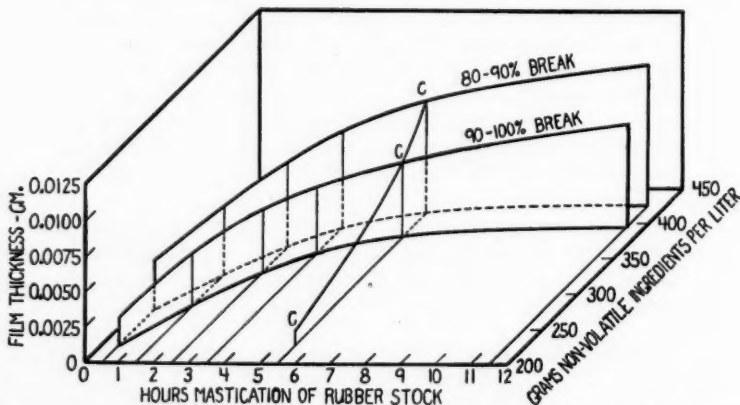bber stock and the concentration of nonvolatile ingredients. Figure 7 shows the relation of film thickness and per cent break to time of mastication of stock and concentration of cement for the benzene cement described which contains 11.2 per cent by volume of isopro-

panol. All data are for 25° C. and 20 per cent relative humidity. For this cement and these conditions:

1. To obtain 0.0025-cm. film thickness and 90–100 per cent break, the rubber stock must be masticated one hour and the cement must contain 250 grams of nonvolatile ingredients per liter. (In mastication, time is measured from the start of the breakdown of crude rubber and includes mixing of pigments. The stock was mixed and masticated on a cold mill. The batch size was 1000 grams. A 12-inch laboratory mill was used with rolls 6 inches in diameter and a differential roll speed of 1.5 to 1 with the front roll speed 20 r. p. m. The mill opening, as measured by the thickness of the rubber sheet, was 0.25 inch. A continuous bank was maintained, and the batch was cut from left to right and folded back every 30 seconds.)

2. To obtain 0.0063-cm. film thickness and 90–100 per cent break, the rubber stock must be masticated 10 hours and the cement must contain 400 grams of nonvolatile ingredients per liter.
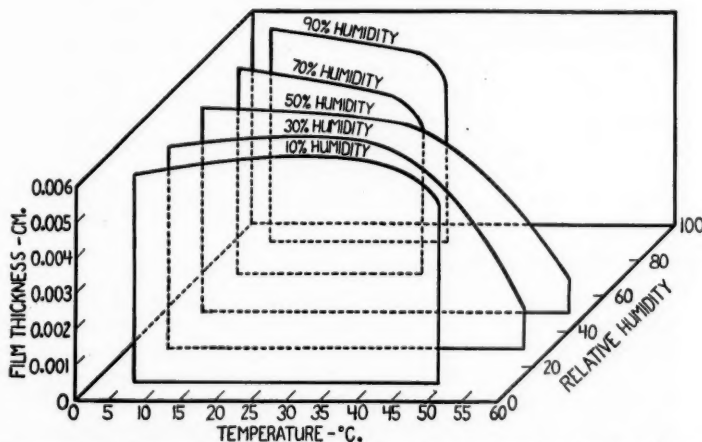
FIGURE 8. RELATION OF FILM THICKNESS OBTAINABLE AT 100 PER CENT BREAK TO TEMPERATURE AND HUMIDITY OF THE DIPPING ROOM FOR A BENZENE-ISOPROPANOL CEMENT CONTAINING 11.2 PER CENT BY VOLUME OF ISOPROPANOL

Rubber stock masticated 5.5 hours.

Physical Chemistry of Film Breaking with Isopropanol

When a film deposited from a benzene-isopropanol cement breaks, it breaks across a tiny pool of clear solvent. These pools can be observed in the process of formation. They occur all over the surface of a film (not just where the film covers a hole), and their craters leave the dried film with a dull appearance.

If a little isopropanol is stirred into benzene, an emulsion is formed. Not until about 50 parts isopropanol per 100 parts benzene have been added is a clear solution obtained. That

is, in concentrations below about 33 per cent by volume, isopropanol does not completely dissolve in benzene.

If for any of the benzene-isopropanol cements the percentage isopropanol in total solvent is calculated for any point where coagulation just occurs (shown by downward arrows in Figures 5 and 6), this value will be very close to 33 per cent.

The suggested explanation of film breaking is that in the film deposited from the cement, as in the cement and in a simple benzene-isopropanol mixture, the isopropanol is in a state of fine dispersion. Since, in the drying film, benzene evaporates more rapidly than isopropanol, the concentration of isopropanol gradually increases until it reaches that point where it is capable of dissolving all of the benzene, and then precipitation of the rubber occurs. The effect is the same whether a given percentage of isopropanol is reached by addition of isopropanol or by evaporation of benzene.

That isopropanol in benzene cements removes a portion of the benzene from its role as solvent might be concluded from the observation that curing cements containing isopropanol are more likely to gel than those which do not contain it, presumably because of greater effective total solids concentration in the benzene remaining free. Furthermore, the fact that such cements which have gelled have a granular appearance suggests at least an incipiently discontinuous liquid system.

Effect of Temperature and Humidity

For a cement of the type used in the preceding experiments the relation of film thickness obtainable at 100 per cent break to the temperature and humidity of the dipping room is shown in Figure 8. The concentration of nonvolatile ingredients necessary to obtain each film thickness shown is given by curve $C C C$ (Figure 7). Figure 8 was simplified from extrapolated data for illustrative reasons. It shows the importance of careful control of temperature and humidity in dipping operations. Evidently for this particular cement a temperature of about 20° C. and moderate humidity would be good working conditions. However, in forming surgeons' gloves where a naphtha cement is used, the temperature of the dipping room is held at about 30° C. and the humidity is very high. Since film thickness and film breaking are both closely related to solvent evaporation rate, it is obvious that, for any cement, optimum temperature and humidity depend upon the nature of the solvents present.

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Hot vs. Cold
Breakdown of Rubber

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The value of, and methods for, breaking down crude rubber have been the subjects of much opinionated discussion among rubber men of many generations. The questions normally center about such points as the kind of equipment and its best adjustment; time, temperature, and sequence of conducting operations; methods of measuring the degree of softness obtained; and the quality of the crude rubber and finished product, both unaged and aged. Time has brought a reasonable unanimity of opinion on some points, for example, the efficacy of a series of short breakdown periods on an open mill, with intermittent intervals of cooling, compared with a single long period of continuous mastication. Among other points not in common agreement, hot vs. cold breakdown takes a prominent position. Here differing viewpoints not only exist between various plants, but between different persons of the same plant and even of the same laboratory.

If an attempt is made to compare results in different plants, one will find it difficult to draw any definite conclusions, owing to differing conditions of physical manipulation and measurements, not the least of which are the various types of plastometers used. Because of this set of conditions the present author was prompted to conduct a series of experiments with the object of obtaining data with which the relative plasticizing effects of different methods of breaking down rubber over the greatest practicable temperature range on both open mills and in internal mixers could be evaluated.

To eliminate all possible variables, smoked sheet with a plasticity of about 95 was used in all cases; the batches were of like size for each individual experiment in a series on a given machine; the period of rest between mixing and making plasticity measurements was the same in all cases, viz., 48 hours; all such measurements were made with a Mooney plastometer, and each sample was brought to 180° F. by the platens of the instrument before testing.

Numerous experiments have been conducted with batches on an open roll mill by different individuals as well as the present author to find a means of raising the temperature of the mass to the region of 390° F. or above, but without success. Even with high-pressure steam in the rolls, radiation was great enough to cause a batch temperature equilibrium well below this level. Any such procedure constitutes one type of so-called "cold breakdown," and where open mills are to be employed it is best to try to keep the rubber as cold as possible by the various means with which all are familiar. Nor is cold breakdown confined to open mills, as will be shown with internal mixer data.

By the term "hot breakdown," is meant temperatures from 390° F. to 400° F. and over. This immediately brings up the question about the aging of this type of rubber. This is better left to the individual rubber chemist, and the author has run no tests to cover the subject. However, the consensus of opinion is that aging, though slightly inferior, is extremely slight and very often hard to find. To offset this, in twenty tests where very hot broken rubber was used to make up a finished article an increase in tensile strength was found. The idea of very hot breakdown

is not new by any means; there are a number of well-known concerns that have been using it for years with excellent results, and have been profiting by the savings by this method.

In breakdown tests on a roll mill, one pound of rubber was used to each inch of mill surface, in other words 60, pounds of smoked sheet on a 60-inch mill. Bank grinding was used; the mills were opened from $1/4$ to $1/2$ inch, and the rubber cut often so that the bank would be actively masticated.

It is generally conceded that the most efficient method of mill breakdown is to run for a short period of about 15 minutes, to allow the rubber to become cold, to return it to the mill for an additional 15 minutes, and to repeat this sequence until the required plasticity is obtained. Table I shows that the drop in plasticity was rapid for the first 15 minutes, from 95 to 73. When the rubber was allowed to remain on the mill, the plasticity values decreased, but the drop was comparatively slow when the rubber reached the maximum temperature. Four 15-minute periods, with 12-hour cooling intervals, give a plasticity of 60; while a straight two-hour run was required to give the same figure. This is definite confirmation of the advisability of cooling when time and temperature equilibrium points are reached.

TABLE I

Plasticity	Time	Cooling Period
73	1st—15 minutes	. . . . . .
67	2nd—15 minutes	12 hours
62	3rd—15 minutes	12 hours
60	4th—15 minutes	12 hours
70	30 minutes	Straight run
60	2 hours	Straight run
55	$2^1/_2$ hours	Straight run
50	3 hours	Straight run
46	$3^1/_2$ hours	Straight run
42	4 hours	Straight run

The next tests were run on a No. 11 Banbury, using 300 pounds of smoked sheet, keeping this in the mixer for 15 minutes, then working the batch on a sheeting mill for an additional 10 minutes. As seen in Table II, there was no reduction in plasticity by working the rubber on the 84-inch mill. The plasticity of the rubber at the end of the 15 minutes' working in the Banbury was the same as after the additional 10 minutes on the 84-inch mill. This again indicates that it is a waste of time, power, and labor to work rubber on a mill after it has reached a maximum temperature. In each of the six batches, the size, the time in the Banbury, and the time on the sheeting mill were the same. The only change was that the cooling

TABLE II

All Batches 300 Pounds and Machine Speeds Standard

Plasticity	Machine	Time (Min.)	Temperature (° F.)
75	#11 Banbury	15	270
75	84″ Sheeter	10	270
79	11 Banbury	15	280
78	84″ Sheeter	10	280
74	#11 Banbury	15	320
74	84″ Sheeter	10	320
71	#11 Banbury	15	345
70	84″ Sheeter	10	345
67	#11 Banbury	15	355
68	84″ Sheeter	10	355
68	#11 Banbury	15	365
71	84″ Sheeter	10	365

water was on during the first two batches and completely off for the last four batches, thus letting the temperature of the rubber rise with each batch. The heat in this case was purely from friction, as no steam or other heating agent was used.

It will be seen that, with all other conditions the same, the plasticity of the rubber decreased directly as the temperature rose. Although the temperature rose steadily after the water was turned off, the temperature would not have gone much above the 365° F., which was attained on the sixth batch, as the temperature rise and the surface radiation would have soon reached equilibrium. It is necessary, therefore, to use some heating medium on a Banbury, or to increase the r. p. m. of the rotors to increase the heat obtained by friction.

Following the above reasoning, a third series of tests was conducted in a No. 3A Banbury, the machine being standard and the rotors turning 34 r. p. m. To increase the temperature of the rubber, 80 pounds' steam pressure was used on the sides, rotors, and door of this unit. Table III gives the results on a steam-heated No. 3A Banbury, standard speed.

In the seven-minute batch, despite the fact that 80 pounds' steam pressure was used on the mixer, the temperature did not exceed 360° F., while the plasticity was 59. This compares with the plasticity at the end of four 15-minute periods, given in Table I and also with that obtained at the end of the straight two-hour run on mills, as shown in the same table. This practice therefore classifies itself as cold breakdown.

TABLE III
All Batches 75 Pounds

Plasticity	Time (Min.)	Temp. (°F.)
68	4¹/₂	310
68	4¹/₂	320
62	7	360
61	7	360
59	7	360

The same mixer was used for a final series of tests, shown in Table IV. The r. p. m. of the rotors was roughly doubled; actually the increase was from 34 to 62. In this test, instead of 80 pounds' steam pressure, only 40 pounds was used, as it was expected that the higher speed would give the required temperature.

TABLE IV
All Batches 75 Pounds, and Speed 62 R. P. M., 3A Banbury Used

Plasticity	Time (Min.)	Temp. (°F.)
62	7¹/₂	328
60	5	340
59	5	350
57	5	380
56	5	370
49	7¹/₂	380
42	7	390
42	7	400
37	12	415

These data show that the increase of speed generated enough frictional heat to reach 400° F. in short order. In seven minutes at this temperature, a plasticity of 42 was obtained, which compared in softness with a continuous run of four hours in the first series of tests, Table I.

The study of temperatures, times, and plasticities as presented in the various tables is an interesting one which points to the possibility of substantial economies in rubber breakdown practice.

It is well to keep in mind that there is seldom need of rubber with plasticity as low as 42 or 37. Usually a softness of 60 to 65 is sufficient. This can be obtained readily in $4^1/_2$ to 7 minutes with a standard Banbury; whereas the softer varieties can be obtained in the same time with rotor speed adjustment.

These experiments have been confined to measurement of the physical results obtained by varying mechanical processes, and have nothing whatsoever to do with the determination of the underlying causes of these plasticity effects.

Rubber Latex for Road Surfacing

W. G. Wren and A. T. Faircloth

The following report is extracted from the first quarterly circular of the Rubber Research Scheme (Ceylon). It is the first interim report on investigations in progress at the Imperial Institute on the utilization of rubber latex for road surfacing, work which is financed by a special grant from the Rubber Research Institute of Malaya.

General Scheme of Investigation

The most promising of a number of methods available for applying latex to roadways is that developed by the Rubber Research Institute, which consists of treatment of latex with aluminous cement. In the first instance attention was, therefore, devoted to this process, bearing in mind that other methods of removing water will eventually require examination. The first step consisted in carrying out experiments to obtain as much fundamental information as possible concerning the physics and chemistry of latex-cement mixtures, with a view to gaining experience and knowledge of value in developing a suitable process.

The following are the directions in which progress has been made during the three months ending August 31, 1936.

(1) Development of a technic for the microscopic examination of latex-cement mixtures, with a view to following the interaction between latex and cement under various conditions and to studying the structure of the dry material. (2) Determination of the extent to which latex is chemically dehydrated by aluminous cement. (3) Study of the effect of a wide range of protective colloids on the setting and mechanical properties of aluminous cement. (4) Study of effect of compounding ingredients and coagulants on the physical properties of unvulcanized latex films. These investigations are still in the preliminary stage, except that dealing with the effect of protective colloids on the hardening and mechanical properties of cement. This investigation has shown that under certain conditions some protective colloids almost entirely prevent the setting and hardening of cement to a coherent mass and that others accelerate it. This information is of considerable practical importance, particularly if at a subsequent stage it is found desirable to prevent the adhesion of cement particles to each other with a view to retaining an elastic structure.

In the course of investigations on the effect of compounding ingredients and coagulants on the properties of dried latex films, a means was found for preparing raw rubber crumb in a very fine condition. It was found possible also to prepare latex-cement mixtures in the form of a crumb which could be pressed under a load of approximately 1000 lbs. per sq. in. to give coherent slabs, which appeared to be stronger and more elastic than those prepared by allowing the latex-cement mixtures to dry *in situ*. The preparation of latex-cement mixtures in crumb form has advantages with respect to ease of laying and reduction of tendency to crack and the properties of this form of mixture will be studied more fully as opportunity occurs.

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(1) Microscopic Technic

Attempts were made to prepare sections for examination by transmitted and reflected light. It was found that grinding at atmospheric temperatures removed particles of cement from the rubber, but smooth surfaces suitable for examination by reflected light could be obtained by grinding with No. 600 carborundum in liquid air. It was not found possible to cut or grind thin sections suitable for examination by transmitted light, even when frozen in liquid air or in solid carbon dioxide. Attempts to prepare sections for examination by reflected light by casting on to glass plates were not successful, owing to the formation of a film of rubber at the surface of the glass plate.

A few preliminary experiments were made with osmic acid, Sudan III, and iodine as staining agents for rubber, and with alizarine for cement. Of these, osmic acid was the least promising, and it is proposed to give the remaining staining agents a more extensive trial and also to experiment with others. It was observed that a solution of alizarine did not stain a mixture of cement in rubber prepared on the mixing rolls, though it stained one prepared from latex.

TABLE I

CLASSIFICATION OF STABILIZERS ACCORDING TO THEIR EFFECT ON ALUMINOUS CEMENT

Those Which Do Not Retard Hardening and in Some Instances Accelerate Both Setting and Hardening and Improve Tensile Strength	Those Which Markedly Retard Hardening	Those Which Show a Marked Slumping Effect in 1 Per Cent Solution	Those Which Have No Slumping Effect in 5 Per Cent Solution	Those Which Markedly Reduce the Tensile Strength of Sand-Cement Mixtures, Especially Using 5 Per Cent Solution
Gum acacia	Saponin	Dextrin	Casein	Saponin
Gum acacia in ammonia	Saponin in ammonia	Gelatin	Starch	Saponin in ammonia
Potash soap	Peptone	Sodium* silicate (crystals)	Agar-agar	Starch
Ammonium stearate	Water glass	Saprotin	Potash soap	Sulfonated lorol
Potassium hydroxide	Saprotin	Darvan powder	Ammonium stearate	Nekal
Bentonite	Darvan powder	Dispersol	Potassium hydroxide	Potash soap
	Gelatin		Bentonite	Sodium silicate (crystals)
				Potassium hydroxide

* Slumping effect only slight with 5 per cent solution.

(2) Chemical Dehydration of Latex by Cement

There is considerable doubt whether cement combines with the whole of the water in latex, particularly that which is associated with the rubber as water of hydration, and it may be difficult to remove this uncombined water by surface evaporation from carpets about 1 inch thick. Rubber which is associated with water is much weaker and less elastic than dry rubber, and is more likely to develop defects at low temperatures. A preliminary experiment showed that there is an appreciable rise in temperature (of about 4° C.) when latex is mixed with cement. This is evidence that cement combines with a portion of the water in latex, which, of course, is not unexpected. More comprehensive experiments have been designed, however, to determine the amount of free and combined water in latex-cement mixings. These will take some time to complete. The problem is a difficult one, owing to the

fact that under such conditions the cement contains water which is in equilibrium with the moisture in the atmosphere, and it may not be possible by chemical methods to determine the amount of water retained by the rubber.

TABLE II

SUMMARY OF 28-DAY TENSILE STRENGTHS OF MIXTURES COMPOSED OF 3 PARTS OF BRITISH STANDARD CEMENT-TESTING SAND TO 1 PART OF CEMENT BY WEIGHT GAGED WITH 1 PER CENT AND 5 PER CENT SOLUTIONS, RESPECTIVELY, OF VARIOUS STABILIZERS, ETC.

	Air		Water	
	1 Per Cent	5 Per Cent	1 Per Cent	5 Per Cent
Control, sand, cement, and water only	488		435	
Do. gaged with 1 per cent NH₄OH	527		407	
1. Casein	395	380	395	440
2. Saponin		Too weak to test		
2ᴀ. Saponin + ammonia (3 per cent)	177	...	...	...
3. Certus Glue	477	417	405	420
4. Sulfonated lorol	473	148	410	143
5. Nekal	407	237	397	170
6. Introsol	463	483	423	457
7. Starch solution	283	203	370	287
8. Peptone	527	...	467	340
9. Lecithin		Not tested		
10. Gum acacia	470	558	452	483
10ᴀ. Gum acacia + ammonia	473	500	412	468
11. Dextrin	212	473	320	443
12. Agar-agar	523	227	417	330
13. Egg albumen	587	550	423	453
14. Gum tragacanth	248	...	387	...
15. Gelatin	490	430	392	400
16. Potash soap	497	268	420	275
17. Ammonium stearate	553	445	407	442
18. Sodium silicate (crystallized)	538	283	383	215
19. Water glass (1.7 d.)	490	375	372	360
20. Saprotin	350	...	338	387
21. Darvan powder	510	350	403	363
22. Potassium hydroxide	422	232	312	293
23. Bentonite	537	340	398	360
24. Dispersol	527	418	405	383

(3) Effect of Latex Stabilizers on the Properties of Cement

When ammonia-preserved latex is mixed with aluminous cement it quickly coagulates unless it is previously treated with a stabilizer. A wide range of materials may be used for this purpose, and owing to their surface effects may have an important influence on the setting and hardening and other properties of cement. A wide range of protective colloids dissolved in water was therefore mixed with fixed proportions of aluminous cement and their effect is shown in Tables I and II. The stabilizers can be divided into three classes (Table I), (1) those which do not retard hardening and in some cases improve the tensile strength of cement, e. g., gum arabic; (2) those which retard hardening and reduce the tensile strength of cement, e. g., saponin; (3) those which have a marked plasticizing effect on the cement, so that in the presence of fixed proportions of water the aqueous cement is much more fluid in the presence of the stabilizer, e. g., saprotin.

It is evident that in future experiments with latex and cement the different effects of the three types of stabilizers will require consideration. For example, it is possible that saponin will yield a more "rubbery" type of material than gum acacia, as it may prevent the cement particles from building up in the form of a continuous cement structure, and saprotin may have advantages in ease of handling.

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(4) Effect of Compounding Ingredients and Coagulants on the Physical Properties of Unvulcanized Latex Films

Previous work had shown that the tensile strength of rubber and cement mixtures prepared from latex and cement is less than the tensile strength of either the cement or the dried latex alone. It was therefore considered to be of importance to determine the effect of materials other than cement which may subsequently be of value in connection with the work. The preparation of films suitable for testing was, however, found to present certain difficulties, chiefly due to the presence of air bubbles, uneven surface, and the settling out of the fillers. Another difficulty which had previously been found to affect the results was the presence of small amounts of residual moisture in the dried film.

A few results have been obtained on the effects of adding carbon black, benzene emulsion, and silica gel to latex. The latter, obtained from water glass by precipitation with acid *in situ*, appears to improve the tensile strength. This is of interest in connection with other problems which have been encountered in these laboratories.

Summary

(1) Methods of preparing sections for microscopical examination have been developed in order to obtain information as to the structure of latex-cement mixtures.

(2) A large range of protective colloids which act as stabilizers of rubber latex have been examined as to their effect on the physical properties of aluminous cement, particularly on the rate of setting and hardening and tensile strength. Important differences in the effects produced by these substances have been found.

(3) The possibilities of preparing a rubber cement crumb for consolidation on the highway are under examination.

(4) A few experiments on the effects of compounding ingredients on the tensile strength of dried latex (without mastication) have been made. Silica gel improves the tensile strength of the dried film.